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Supporting Information

Flexible Alkylene Bridges as a Tool To Engineer Crystal Distyrylbenzene Structures Enabling Highly Fluorescent Monomeric Emission

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1. General procedure

^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER 500 (125 MHz) spectrometers or JEOL 400 (100 MHz) spectrometers for $CDCl_3$ solutions using tetramethylsilane (TMS) as an internal standard. Date for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constants (Hz). ^{13}C NMR spectra were reported as chemical shifts in ppm and multiplicity where appropriate. Melting points were recorded on a METTLER TOLEDO FP82HT Hot stage controlled with the METTLER TOREDO Central Processor of the FP900 System. Recycling HPLC was performed at room temperature using a JAI LC-9204 Recycling Preparative HPLC with a refractive index (RI) detector: RI-50s and a UV detector: S-310 A model II controlled with TECHNO ALPHA Smart Chrom system.

UV-Vis spectra were recorded on a JASCO V-670 UV-vis spectrophotometer, and fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. The wavelengths obtained by the fluorescence spectrometer were converted to wavenumber using the equation $I(\tilde{\nu}) = \lambda^2 I(\lambda)^4$. Absolute quantum yields were measured by a Hamamatsu Photonics Quantaurus QY apparatus.

All photophysical measurements were performed using dilute solutions with optical densities (ODs) around 0.1 at the maximum absorption wavelength in 1 cm path length quartz cells at room temperature (298 K). In addition, all sample solutions were deaerated by bubbling with argon gas for 15 min prior to the quantum yield.

Emission lifetimes were obtained using a Horiba FluoroCube time-correlated single-photon counting system. The excitation light sources were LED pulse lamps (NanoLED, 269 nm and 379 nm). The solution samples were dissolved in THF and purged with argon for 20 minutes before lifetime measurements. In all samples, the time-to-amplitude converter ranges were 50 ns, and the amounts of counts were 10000. Reptation rates were 1 MHz in solution samples and 100 kHz in solid samples.

Diffuse-reflectance spectra were recorded on a JASCO FP-6500 spectrofluorometer equipped with an integration sphere detector. Thus, the experimental error arising from the fluorescence, typically encountered with diffuse-reflectance spectrometers producing polychromatic outgoing light, was avoided. Samples and references were charged in a JASCO powder sample cell to obtain a sufficiently thick powder layer. Just before each measurement, the synchronous spectrum of the NaBr powder was measured as a reflectance spectrum of a standard reference $r_{\text{standard}}(\lambda)$. Then, a reflectance spectrum of each sample $r_{\text{sample}}(\lambda)$ was obtained following the same procedure. In addition to neat powder samples, the spectra of samples adsorbed on the NaBr powder were measured at a concentration of 1.0×10^{-3} M. The obtained reflectance spectra $r_{\text{sample}}(\lambda)$ and $r_{\text{standard}}(\lambda)$

were converted to Kubelka–Munk functions $f(r_\infty)$ using the following equation:

$$f(r_\infty) = \frac{\left(1 - r_\infty(\lambda)\right)^2}{2r_\infty(\lambda)}, \text{where } r_\infty(\lambda) = \frac{r_{\text{sample}}(\lambda)}{r_{\text{standard}}(\lambda)}$$

All diffuse-reflectance spectra are displayed at plots of the Kubelka-Munk functions, *i.e.*, $f(r_\infty)$ as a function of the wavelength, λ.

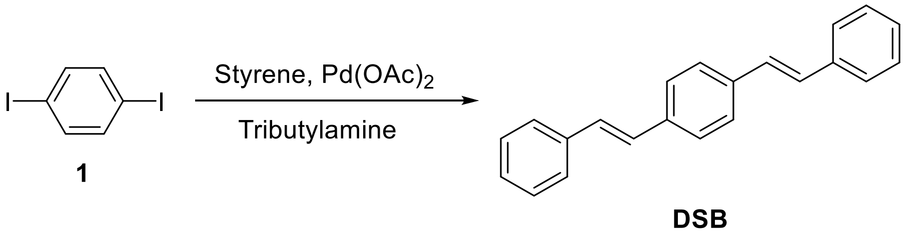
Single crystal X-ray structural analysis were obtained using a Rigaku AFC10 with Saturn 70 CCD detector (for **DBDMDB[7]**, **DBαMDB[7]-cross/parallel**, and **5DBαMDB[7]**) and a Rigaku FR-E+ with Hypix-6000 area detector (for **DSDMB**, **DBDB[6]**, **DBDB[7]** and ***t*BuDBαMDB[7]**). The single crystals of **DSDMB**, **DBDB[6]**, **DBDB[7]** were made from a mixed solvent of dichloromethane and methanol, and that of **DBDMDB[7]**, **DBαMDB[7]-cross/parallel**, **5DBαMDB[7]**, and ***t*BuDBαMDB[7]** were made from a mixed solvent of dichloromethane and hexane evaporated gradually under atmospheric conditions.

2. Materials

All solvents and chemicals were commercially available and used without further purification unless otherwise noted. Column chromatography was performed on silica gel (Silica Gel 60N, 63-210 μm, Kanto Chemical Co., Inc.). 1,4-Diiodobenzene, styrene, tributylamine, palladium(II) acetate, 1,4-diiodo-2,5-dimethylbenzene, potassium *tert*-butoxide, *α*-methylstyrene, tri(*o*-tolyl)phosphine, triethylamine, *β*-tetralone, *N*-phenylbis(trifluoromethanesulfonimide), 1,4-benzendiboronic acid bis(pinacol)ester, tetrakis(triphenylphosphine)palladium(0), 2,5-dibromo-*p*-xylene, bis(pinacolato)diboron, [1,1-bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane adduct, methyltriphenylphosphonium bromide, α-tetralone, ethyltriphenylphosphonium bromide, [hydroxy(tosyloxy)iodo]benzene, 6-bromo-1-tetralone, ethyltriphenylphosphonium iodide, 1-pentene, ethylene glycol, *p*-toluensulphonic acid monohydrate, 2-chloro-2-methylpropane, and ammonium chloride were purchased from TCI (Tokyo, Japan). Tripotassium phosphate (K_3PO_4), *N*,*N*-dimethylformamide, ethanol, toluene, chloroform, methanol, 1,4-dioxane, ethyl acetate, hexane, tetrahydrofuran, and diethyl ether were purchased from Kanto Chem (Tokyo, Japan). 9-Borabicyclo 3.3.1 nonane 0.5M tetrahydrofuran, 1,3-dicyclohexylimidazolium tetrafluoroborate salt, and magnesium sulfate were purchased from Sigma-Aldrich Japan (Tokyo, Japan). Sodium hydroxide, magnesium, celite, and sodium hydrogen carbonate were purchased from Nacalai Tasque (Kyoto, Japan). Potassium acetate and nickel(II) chloride hexahydrate were purchased from Wako Pure Chem (Tokyo, Japan). Methylene chloride was purchased from AGC Chemicals (Tokyo, Japan). Spectrograde solvent (tetrahydrofuran) was purchased from Nacalai Tesque (Kyoto, Japan) and Wako Pure Chem (Tokyo, Japan).

3. Synthesis and characterization

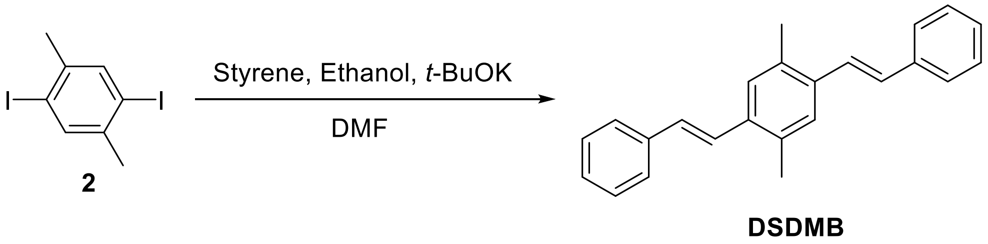
(1) Synthesis of 1,4-di((*E*)-styryl)benzene (**DSB**)[1]



Scheme S1. Synthesis of **DSB**.

A mixture of 1,4-diiodobenzene (**1**) (0.66 g, 2.0 mmol), styrene (0.57 mL, 5.0 mmol), and $Pd(OAc)_2$ (0.01 g, 0.04 mmol) was dissolved in tributylamine (0.95 mL, 4.0mmol). The reaction mixture was refluxed at 100°C for 1 day. The mixture solidified during the heating. The solid reaction mixture was broken up with a spatula and stirred with water. The solid was filtered, washed several times with fresh water, and filtered through Celite by hot DMF. Recrystallization from hot DMF and adding water until crystals began to appear in the hot filtrate gave **DSB** as a pale green solid. Yield:48%; Mp: 257.0°C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 9.0 Hz, 8H), 7.37 (t, J = 7.5 Hz, 4H), 7.28 (s, 2H), 7.13 (t, J = 17.5 Hz, 4H) (**Figure S40**).

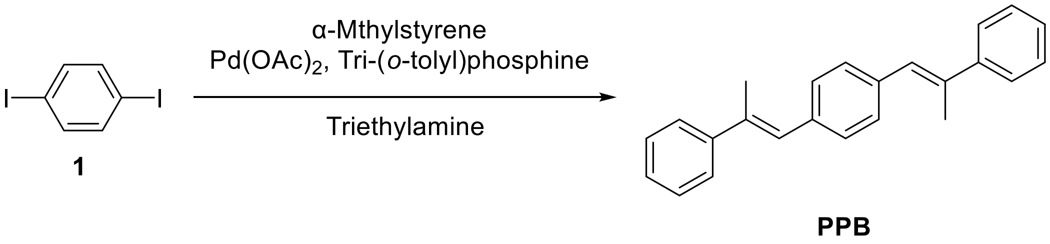
(2) Synthesis of ((1*E*,1'*E*)-(2,5-dimethyl-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene (**DSDMB**)[2]



Scheme S2. Synthesis of **DSDMB**.

A mixture of 1,4-diiodo-2,5-dimethylbenene (**2**) (0.71 g, 2.0 mmol), styrene (2.29 mL, 20.0 mmol), potassium *tert*-butoxide (1.35 g, 12.0 mmol) and ethanol (0.05 mL, 0.9 mmol) was dissolved in DMF (10 mL) under argon atmosphere. The mixture was refluxed at 80°C for 6 hours, then cooled to room temperature. Water was added to the solution, and the mixture was extracted with diethyl ether. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a residue. The residue was chromatographed over silica gel, eluted with toluene, and recrystallized from 3/1 (v/v) methanol/chloroform to give **DSDMB** as a pale-yellow solid. Yield: 6%; Mp: 196.7°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 4H), 7.44 (s, 2H), 7.37 (t, *J* = 7.3 Hz, 4H), 7.32 (d, *J* = 16.2 Hz, 2H), 7.27 (d, *J* = 10.1 Hz, 2H), 7.03 (d, *J* = 15.9 Hz, 2H), 2.44 (s, 6H) (δ 2.17 is the peak of acetone, mixed with $CDCl_3$) (**Figure S41**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.9, 135.7, 133.7, 129.6, 128.8, 127.7, 127.3, 126.7, 126.3, 19.7 (**Figure S42**).

(3) Synthesis of 1,4-bis((*E*)-2-phenylprop-1-en-1-yl)benzene (**PPB**)[3]

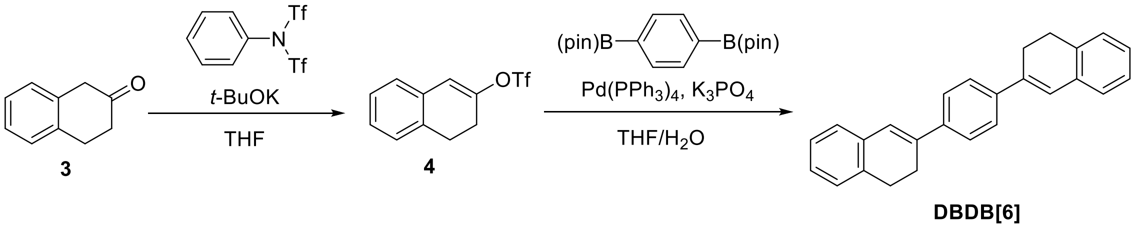


Scheme S3. Synthesis of **PPB**.

α-Methylstyrene (1.95 mL, 15.0 mmol), 1,4-diiodobenzene (**1**) (1.65 g, 5.0 mmol), $Pd(OAc)_2$ (0.02 g, 0.09 mmol) and tri-(*o*-tolyl)phosphine (0.06 g, 0.2 mmol) was added in triethylamine (4.16 mL) in thick glass tube sealed with screw cap and stirred at 130°C for 1 day. Water was added to the solution, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a residue. The residue was chromatographed over silica gel, eluting with 3/1 (v/v) hexane/dichloromethane, and recrystallized from dichloromethane to give **PPB** as a pale green solid. Yield: 25%; Mp: 172.9°C; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.55-7.53 (m, 4H), 7.40-7.37 (m, 8H), 7.30 (t, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 0.9 Hz, 2H), 2.34 (s, 6H) (**Figure S43**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.2, 137.6, 136.7, 129.2, 128.5, 127.7, 127.3, 126.2, 17.8 (**Figure S44**).

PPB included small amounts of contamination (see in **Figure S43**). Thus, we measured absorption and fluorescence spectra of **PPB** in 80% water suspensions (**Figure S10**) to compare with the reported result[4]. As a result, λ_{abs} was almost the same and fluorescence spectra had a similar trend to the reported result, and we determined that using this **PPB** was no problem.

(4) Synthesis of 1,4-bis(3,4-dihydronaphthalen-2-yl)benzene (**DBDB[6]**)



Scheme S4. Synthesis of **DBDB[6]**.

3,4-Dihydronaphthalen-2-yl trifluoromethansulfonate (**4**)[5]

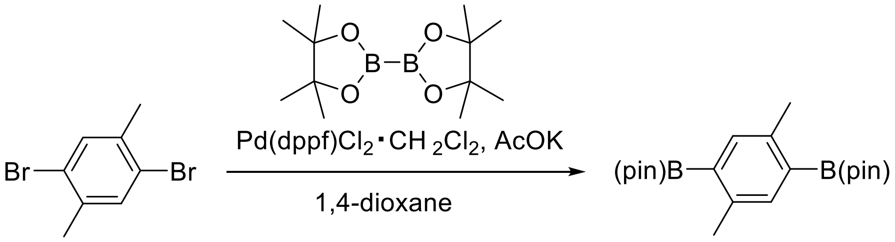
β-Tetralone (**3**, 1.5 g, 10 mmol) was dissolved in THF (30 mL) under an argon atmosphere. The reaction mixture was cooled to -20 °C, and potassium *tert*-butoxide (1.5 g, 13 mmol) was added to the mixture and stirred at 0 °C for 1 hour. The mixture was cooled to -20 °C, and *N*-phenylbis(trifluoromethanesulfonimide) (4.6 g, 13 mmol) was added to the mixture and stirred at -20 °C for 1 hour, and then stirred at 0 °C for 4 hours. Water was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water and saturated with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a residue. The residue was chromatographed over silica gel, eluting with 4/1 (v/v) hexane/ethyl acetate to give crude **4** as a colorless oil. Yield: 95%; 1H-NMR (399 MHz, $CDCl_3$) δ 7.21-7.19 (m, 2H), 7.16-7.13 (m, 1H), 7.10-7.06 (m, 1H), 6.48 (s, 1H), 3.06 (t, J = 8.2 Hz, 2H), 2.69 (t, J = 8.5 Hz, 2H) (**Figure S45**).

1,4-Bis(3,4-dihydronaphthalen-2-yl)benzene (**DBDB[6]**)[6]

A mixture of **4** (1.2 g, 4.0 mmol), 1,4-benzenendiboronic acid bis(pinacol) ester (0.60 g, 1.8 mmol), K_3PO_4 (2.6 g, 12 mmol), and $Pd(PPh_3)_4$.. (0.23 g, 0.20 mmol) was dissolved in 5/1 (v/v) THF/water (20 mL) under argon atmosphere. The reaction mixture was refluxed at 50 °C for 2 hours and then cooled to room temperature. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a residue. The residue was recrystallized from 1/4 (v/v) hexane/dichloromethane to give **DBDB[6]** as a yellowish solid. Yield: 68%; Mp: 243.2°C; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.57 (s, 4H), 7.22-7.13 (m, 8H), 6.91 (s, 2H), 2.97 (t, J = 8.2 Hz, 4H), 2.78 (t, J = 8.2 Hz, 4H) (**Figure S46**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.1, 138.3, 135.0, 134.9, 127.4, 127.1, 126.8, 125.3, 124.3, 28.3, 26.3 (**Figure S47**); HRMS (EI) Calcd for $C_{26}H_{22}$: 334.1722, Found 344.1723 (**Figure S72**).

(5) Synthesis of 2,2'-(2,5-dimethyl-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-

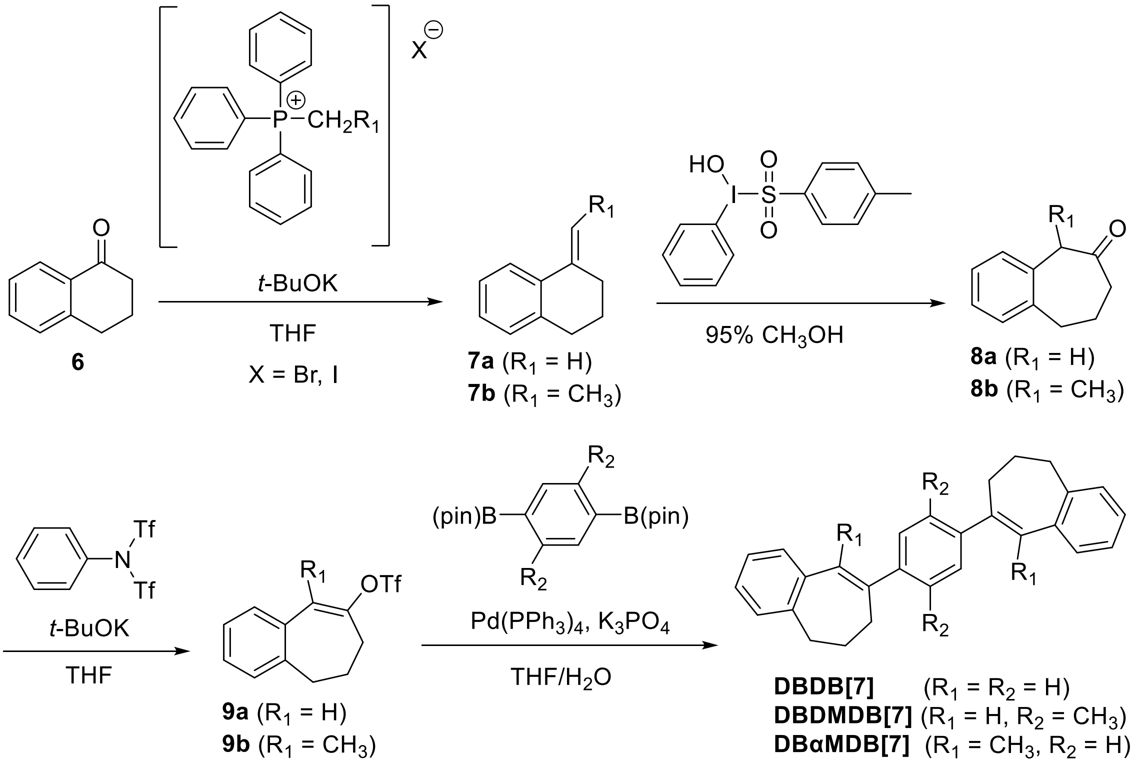
dioxaborolane) (**DMB-B(pin)**)[7]



Scheme S5. Synthesis of **DMB-B(pin)**.

A mixture of 2,5-dibromo-*p*-xylene (**5**) (1.32 g, 5.0 mmol), bis(pinacolate)diboron (3.26 g, 10.0 mmol), potassium acetate (1.47 g, 15.0 mmol) and Pd(dppf)Cl_2 · CH_2Cl_2 (0.12 g, 0.15 mmol) was dissolved in 1,4-dioxane (35 mL) under argon atmosphere. The reaction mixture was refluxed at 80 °C overnight. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over MgSO4, filtered, and evaporated under reduced pressure to give a residue. The residue was chromatographed over silica gel, eluting with 1/2 (v/v) hexane/dichloromethane, and recrystallized from 3/1 (v/v) hexane/dichloromethane to give **DMB-B(pin)** as a colorless solid. Yield: 45%; ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.53 (s, 2H), 2.48 (s, 6H), 1.34 (s, 24H) (**Figure S48**).

(6) Synthesis of **DBDB[7]**s



Scheme S6. Synthesis of **DBDB[7]**, **DBDMDB[7]**, and **DBαMDB[7]**.

1-Methylene-1,2,3,4-tetrahydronaphthalene (**7a**)[8]

Methyltriphenylphosphonium bromide (8.0 g, 22.3 mmol) was dissolved in THF (50 mL) under an argon atmosphere and stirred at 0 °C. Potassium *tert*-butoxide (1.7 g, 22.1 mmol), and α-tetralone (**6**, 1.99 mL, 15.0 mmol) were added to the mixture and stirred at room temperature for 1 hour. Saturated aqueous NH_4Cl was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a residue. The residue was chromatographed over silica gel, eluting with 3/1 (v/v) hexane/dichloromethane to give crude **7a** as colorless oil. Yield: 85%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 1H), 7.18-7.13 (m, 2H), 7.10 (d, J = 7.3 Hz, 1H), 5.48 (s, 1H), 4.95 (s, 1H), 2.85 (t, J = 6.1 Hz, 2H), 2.55 (t, J = 5.8 Hz, 2H), 1.91-1.86 (m, 2H) (**Figure S49**).

1-Ethylidene-1,2,3,4-tetrahydronaphthalene (**7b**)

Following a similar procedure used for the synthesis of **7b** from ethyltriphenylphosphonium Iodide (6.16g, 14.7 mmol) and α-tetralone (**6**, 1.33 mL, 10.0 mmol) stirred at room temperature for 4 hours, chromatographey over silica gel, eluting with 4/1 (v/v) hexane/dichloromethane gave crude **7b** as a colorless oil. Yield: 97%;^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.57-7.55 (m, 1H), 7.42 (dt, J = 8.5, 3.4 Hz, 0H), 7.18-7.07 (m, 3H), 6.14-6.08 (m, 1H), 5.57 (q, J = 7.3 Hz, 0H), 2.83 (t, J = 6.6 Hz, 1H), 2.76 (t, J = 6.2 Hz, 1H), 2.50 (t, J = 6.4 Hz, 1H), 2.43-2.39 (m, 1H), 1.93-1.79 (m, 5H) (**Figure S50**) (**7b** was a mixture of *E* and *Z* configuration).

5,7,8,9-Tetrahydro-6*H*-benzo[7]annulen-6-one (**8a**)[9]

7a (1.83 g, 12.7 mmol) was dissolved in 95% methanol (60 mL), and [hydroxy(tosyloxy)iodo]benzene (5.01 g, 12.8 mmol) was added. The solid dissolved evolution of heat rapidly to a yellow solution. The solution was stirred at room temperature for 20 min, and the solvent was removed in *vacuo*. Dichloromethane and water were added, and the mixture was extracted with dichloromethane. The organic layer was washed with water and brine three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a residue. The residue was chromatographed over silica gel, eluting with 3/1 (v/v) hexane/ethyl acetate to give crude **8a** as a colorless oil. Yield: 84%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.22-7.14 (m, 4H), 3.73 (s, 2H), 2.95 (t, J = 6.3 Hz, 2H), 2.57 (t, J = 6.9 Hz, 2H), 2.02-1.97 (m, 2H) (**Figure S51**).

5-Methyl-5,7,8,9-tetrahydro-6H-benzo[7]annulen-6-one (**8b**)

Following a similar procedure used for the synthesis of **8a** from **7b** (1.36 g, 8.6 mmol), chromatography over silica gel, eluting with 3/1 (v/v) hexane/ethyl acetate gave crude **8b** as a colorless oil. Yield: 69%;^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.24-7.18 (m, 3H), 7.16-7.10 (m, 1H), 3.88 (q, *J* = 7.2 Hz, 1H), 2.97 (qd, *J* = 7.3, 4.6 Hz, 1H), 2.87-2.80 (m, 1H), 2.68-2.63 (m, 1H), 2.48 (qd, *J* = 5.9, 4.2 Hz, 1H), 2.09-2.04 (m, 1H), 1.98-1.87 (m, 1H), 1.45 (d, *J* = 6.9 Hz, 3H) (**Figure S52**) (The compound was a mixture of ketone and acetal (11:5))

6,7-Dihydro-5*H*-benzo[7]annulen-8-yl trifluoromethanesulfonate (**9a**)

Following a similar procedure used for the synthesis of **4** from **8a** (1.70 g, 10.6 mmol), THF (30 mL), potassium *tert*-butoxide (1.58g, 14.1mmol), and *N*-phenylbis(trifluoromethansesulfonimide) (4.95 g, 14.1 mmol), chromatography over silica gel, eluting with 6/1 (v/v) hexane/ethyl acetate, gave crude **9a** as a colorless oil. Yield: 93%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.21-7.16 (m, 3H), 7.11 (t, *J* = 4.1 Hz, 1H), 6.59 (s, 1H), 2.89 (t, *J* = 4.9 Hz, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 2.02-1.97 (m, 2H) (**Figure 53**) (The compound was a mixture of **7a** and N-phenylbis(trifluoromethanesulfonimide (5:1))

9-Methyl-6,7-dihydro-5H-benzo[7]annulen-8-yl trifluoromethanesulfonate (**9b**)

Following a similar procedure used for the synthesis of **4** from **8b** (1.16 g, the amount of ketone = 4.4 mmol), chromatography over silica gel, eluting with 6/1 (v/v) hexane/ethyl acetate, gave crude **9b** as a colorless oil. Yield: 41%; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.24-7.21 (m, 2H), 2.69 (t, J = 6.6 Hz, 2H), 2.32-2.22 (m, 4H), 2.17 (s, 3H) (**Figure S54**).

1,4-Bis(6,7-dihydro-5*H*-benzo[7]annulen-8-yl)benzene **(DBDB[7])**

Following a similar procedure used for the synthesis of **DBDB[6]** from **9a** (0.90 g, 3.1 mmol) refluxed at 60 °C overnight, chromatography over silica gel, eluting with 9/1 (v/v) hexane/dichloromethane, and recrystallization from 3/1 (v/v) hexane/dichloromethane gave **DBDB[7]** as a yellowish solid. Yield: 17%; Mp: 181.2 °C; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.52 (s, 4H), 7.26-7.21 (m, 4H), 7.19 (d, *J* = 6.4 Hz, 2H), 7.17-7.13 (m, 2H), 6.86 (s, 2H), 2.83 (t, *J* = 6.2 Hz, 4H), 2.67 (t, *J* = 6.9 Hz, 4H), 2.27-2.21 (m, 4H) (**Figure S55**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.9, 142.5, 141.4, 137.6, 130.5, 129.1, 128.5, 126.7, 126.2, 126.1, 34.4, 32.4, 30.9 (**Figure S56**); HRMS (EI) Calcd for $C_{28}H_{26}$: 362.2035, Found 362.2028 (**Figure S73).**

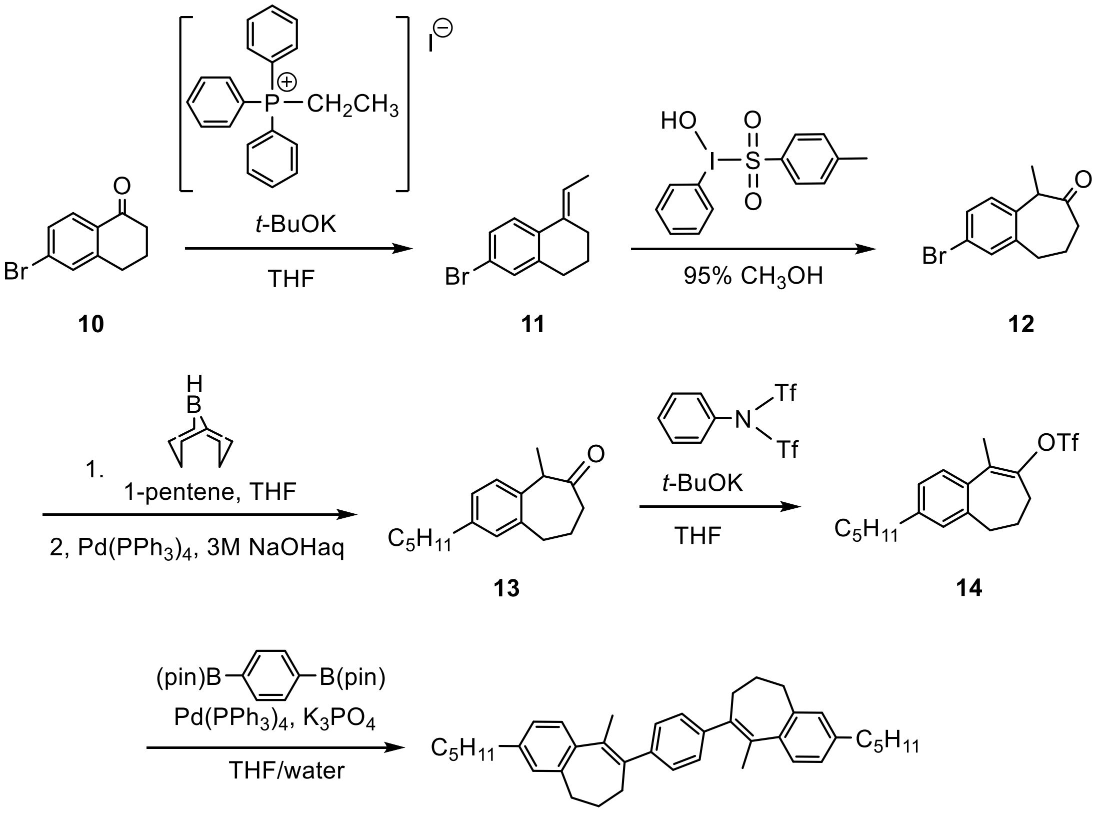
8,8'-(2,5-Dimethyl-1,4-phenylene)bis(6,7-dihydro-5*H*-benzo[7]annulene)

(DBDMDB[7])

Following a similar procedure used for the synthesis of **DBDB[6]** from **9a** (0.90 g, 3.1 mmol) and **DMB-B(pin)** (0.50 g, 1.4 mmol), refluxed at 50°C overnight, chromatography over silica gel, eluting with 9/1 (v/v) hexane/dichloromethane, and recrystallization from 2/1 (v/v) hexane/dichloromethane gave **DBDMDB[7]** as a colorless solid. Yield: 55%; Mp: 156.9 °C; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.21-7.11 (m, 8H), 7.06 (s, 2H), 6.41 (s, 2H), 2.94-2.91 (m, 4H), 2.55 (t, *J* = 6.4 Hz, 4H), 2.34 (s, 6H), 2.20-2.13 (m, 4H) (**Figure S57**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.4, 144.3, 141.4, 136.9, 131.9, 130.7, 130.3, 129.9, 129.2, 126.6, 126.1, 36.2, 35.4, 29.3, 19.6 (**Figure S58**); HRMS (EI) Calcd for $C_{30}H_{30}$: 390.2348, Found 390.2351 (**Figure S74**).

1,4-Bis(9-methyl-6,7-dihydro-5*H*-benzo[7]annulen-8-yl)benzene **(DBαMDB[7])**

Following a similar procedure used for the synthesis of **DBDB[6]** from **9b** (0.31 g, 1.0 mmol) refluxed at 50 °C for 1.5 hour, chromatography over silica gel, eluting with 9/1 (v/v) hexane/dichloromethane, and recrystallization from 3/1 (v/v) methanol/dichloromethane gave **DBαMDB[7]** as a colorless solid. Yield: 49%; Mp: 163.3 °C; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.37 (dd, J = 7.8, 0.9 Hz, 2H), 7.31-7.27 (m, 6H), 7.23 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.19 (td, *J* = 7.1, 1.4 Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 4H), 2.20 (m, 8H), 2.10 (s, 6H) (**Figure S59**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.6, 142.0, 140.3, 137.9, 131.8, 128.6, 128.3, 126.6, 126.2, 34.7, 32.9, 32.2, 20.1 (**Figure S60**); HRMS (EI) Calcd for $C_{30}H_{30}$: 390.2348, Found 390.2350 (**Figure S75**)



Scheme S7. Synthesis of **5DBαMDB[7]**.

6-Bromo-1-ethylidene-1,2,3,4-tetrahydronaphthalene (**11**)

Following a similar procedure used for the synthesis of **7a** from ethyltriphenylphosphonium iodide (6.15 g, 14.7 mmol) and 6-bromo-1-tetralone (**10**, 2.27 g, 10.1 mmol) stirred at room temperature for 4 hours, chromatography over silica gel, eluting with 3/1 (v/v) hexane/dichloromethane, gave crude **11** as colorless oil. Yield: 90%; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.28-7.24 (m, 1H), 7.22 (s, 1H), 6.09 (q, *J* = 7.0 Hz, 1H), 2.71 (t, *J* = 6.2 Hz, 2H), 2.47 (t, *J* = 6.4 Hz, 2H), 1.90-1.74 (m, 5H) (**Figure S61**) (**11** was a mixture of *E* and *Z* configuration).

2-Bromo-5-methyl-5,7,8,9-tetrahydro-6H-benzo[7]annulen-6-one (**12**)

Following a similar procedure used for the synthesis of **8a** from **11** (2.15 g, 9.1 mmol), chromatography over silica gel, eluting with 3/1 (v/v) hexane/ethyl acetate, gave crude **12** as colorless solid: Yield: 74%; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.30 (d, *J* = 1.8 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 3.82 (q, *J* = 7.0 Hz, 1H), 2.97-2.90 (m, 1H), 2.82-2.76 (m, 1H), 2.65 (td, *J* = 11.1, 7.2 Hz, 1H), 2.51-2.45 (m, 1H), 2.13-2.02 (m, 1H), 1.97-1.86 (m, 1H), 1.43 (d, *J* = 7.3 Hz, 3H) (**Figure S62**).

5-Methyl-2-pentyl-5,7,8,9-tetrahydro-6H-benzo[7]annulen-6-one (**13**)[10]

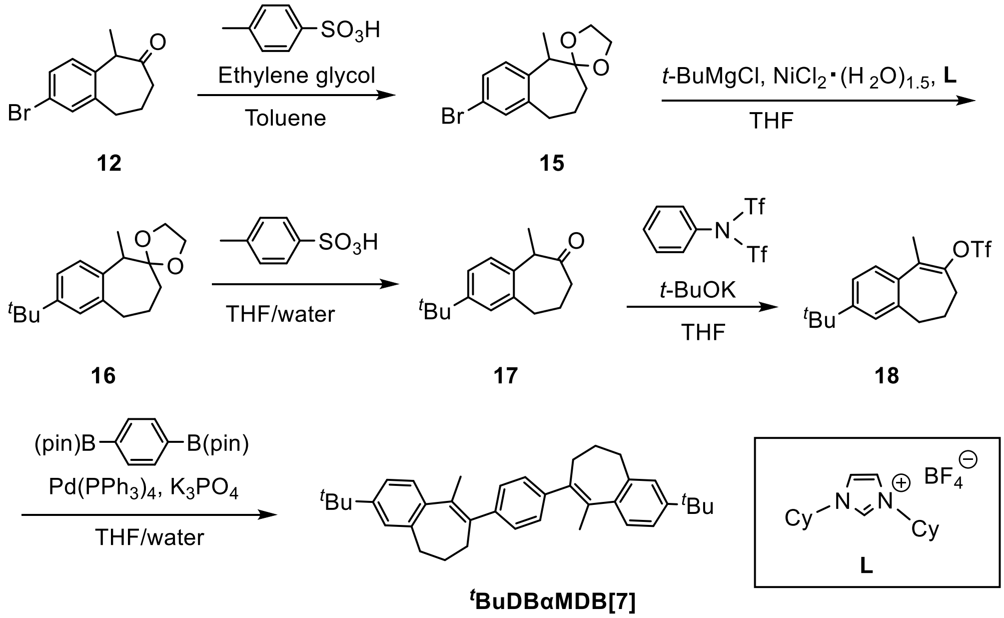
0.5 M 9-BBN in THF (9.8 mL) was stirred at 0°C under argon atmosphere. 1-Pentene (0.54 mL, 4.9 mmol) was added in the mixture and stirred room temperature for 4 hours. Then, 3M aqueous NaOH (3.0 mL), **12** (0.81 g, 3.2 mmol), and $Pd(PPh_3)_4$ (0.13 g, 0.1 mmol) was added in the mixture and refluxed overnight at 70°C. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated to give residue. The residue was chromatographed over silica gel, eluting with 6/1 (v/v) hexane/ethyl acetate to give crude **13** as yellow oil. Yield: 77%; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.8 Hz, 1H), 7.06-7.04 (m, 1H), 6.95 (s, 1H), 3.86 (q, *J* = 7.2 Hz, 1H), 2.98-2.91 (m, 1H), 2.84-2.77 (m, 1H), 2.66 (td, *J* = 11.1, 7.2 Hz, 1H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.50-2.45 (m, 1H), 2.13-2.02 (m, 1H), 1.96-1.85 (m, 1H), 1.64-1.57 (m, 2H), 1.44 (d, *J* = 7.3 Hz, 3H), 1.37-1.29 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H) (**Figure S63**).

9-Methyl-3-pentyl-6,7-dihydro-5H-benzo[7]annulen-8-yl trifluoromethanesulfonate (**14**)

Following a similar procedure used for the synthesis of **4** from **13** (0.60 g, 2.5 mmol), chromatographed over silica gel, eluting with 6/1 (v/v) hexane/ethyl acetate, gave crude **14** as colorless oil. Yield: 63%; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 2.66 (t, *J* = 6.6 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.28-2.24 (m, 4H), 2.14 (s, 3H), 1.66-1.58 (m, 2H), 1.35-1.32 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H) (**Figure S64**).

1,4-Bis(9-methyl-3-pentyl-6,7-dihydro-5H-benzo[7]annulen-8-yl)benzene (**5DBαMDB[7]**)

Following a similar procedure used for the synthesis of **DBDB[6]** from **14** (0.59 g, 1.6 mmol) refluxed at 50°C for 3 hours, chromatography over silica gel, eluting with 9/1 (v/v) hexane/dichloromethane, and recrystallization from 3/1 (v/v) methanol/dichloromethane gave **5DBαMDB[7]** as colorless solid. Yield: 67%; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.25 (d, *J* = 9.6 Hz, 6H), 7.08 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.02 (s, 2H), 2.65 (t, *J* = 6.6 Hz, 4H), 2.58 (t, *J* = 7.8 Hz, 4H), 2.21-2.13 (m, 8H), 2.05 (s, 6H), 1.67-1.60 (m, 4H), 1.37-1.32 (m, 8H), 0.89 (t, *J* = 6.6 Hz, 6H) (**Figure S65**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.1, 141.4, 140.9, 140.2, 137.6, 131.9, 128.7, 128.3, 126.5, 126.1, 35.9, 34.8, 33.0, 32.3, 31.9, 31.4, 22.7, 20.2, 14.2 (**Figure 66**); HRMS (FAB) Calcd for $C_{40}H_{50}$: 530.3913, Found 530.3923 (**Figure S76**).



Scheme S8. Synthesis of **^{t}Bu DBαMDB[7]**.

2-Bromo-5-methyl-5,7,8,9-tetrahydrospiro[benzo[7]annulene-6,2'-[1,3]dioxolane] (**15**)

12 (1.70 g, 6.7 mmol), *p*-toluenesulfonic acid monohydrate (0.46 g, 2.4 mmol) and ethylene glycol (15 ml) was dissolved in Toluene (100 ml) and refluxed at 130°C for 1 day. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give residue. The residue was chromatographed over silica gel, eluting with 3/1 (v/v) hexane/ethyl acetate to give crude **15** as colorless solid. Yield: 60%; ^{1}H-NMR (399 MHz, $CDCl_3$) δ 7.26-7.24 (m, 1H), 7.21 (s, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 3.96-3.89 (m, 4H), 3.05 (q, *J* = 7.3 Hz, 1H), 2.94-2.87 (m, 1H), 2.75-2.70 (m, 1H), 2.07-2.00 (m, 1H), 1.84-1.66 (m, 3H), 1.35 (d, *J* = 6.9 Hz, 3H) (**Figure S67**)

$NiCl_2$ ・ $(H_2O)_{1.5}$[11]

NiCl2 ・ (H2O)6 (2.0 g, 8.4 mmol) was finely ground using a mortar and pestle and transferred to a 50 ml round bottom flask containing a stir chip. The flask was place under high vacuum, and stirred at 100°C for 20 minutes, then 120°C for 10 minutes to give NiCl2 ・ (H2O)1.5. For more information, see Ref[11].

2-(*tert*-Butyl)-5-methyl-5,7,8,9-tetrahydrospiro[benzo[7]annulene-6,2'-[1,3]dioxolane] (**16**)[11]

15 (1.50 g, 5.0 mmol), $NiCl_2$ ・ $(H_2O)_{1.5}$ (0.08 g, 0.5 mmol) and 1,3-

dicyclohexylimidazolium tetrafluoroborate salt (0.18 g, 5.6 mmol) was added into 30 ml 2neck flask under argon atmosphere and stirred at -10°C. 1M *tert*-butylmagnesium chloride in THF (10 ml) was added in the mixture, and stirred at -10°C for 1.5 hours. Ice and saturated aqueous NH_4Cl was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give residue. The residue was chromatographed over silica gel, eluting with 4/1 (v/v) hexane/ethyl acetate, but the resulting compound remained much unreacted **15**, so the same reaction was performed again. The resulting compound (1.25 g, 10/7 (mol/mol) Br/^{t}Bu), **15** (0.30 g, 1.0 mmol), $NiCl_2$・($H_2O_{1.5}$ (0.05 g, 0.3 mmol), 1,3-dicyclohexylimidazolium tetrafluoroborate salt (0.10 g, 0.3 mmol) and 1M *tert*-butylmagnesium chloride in THF (6 ml) were used. Crude **16** as a colorless solid was obtained. Yield: 40%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.14 (dd, J = 7.9, 1.8 Hz, 1H), 7.05 (dd, J = 5.0, 2.9 Hz, 2H), 4.00-3.89 (m, 4H), 3.07 (q, J = 7.3 Hz, 1H), 2.96-2.88 (m, 1H), 2.80-2.75 (m, 1H), 2.07-2.01 (m, 1H), 1.83-1.68 (m, 3H), 1.36 (d, J = 7.6 Hz, 3H), 1.29 (s, 9H) (some amounts of **15** and isomerization product were remained) (**Figure S68**)

2-(*tert*-Butyl)-5-methyl-5,7,8,9-tetrahydrospiro[benzo[7]annulene-6,2'-[1,3]dioxolane] (**17**)

16 (0.66 g, 2.4 mmol) and *p*-toluenesulfonic acid monohydrate (0.2 g, 1.0 mmol) were dissolved in 3/1 (v/v) THF/water (50 ml) and refluxed at 50°C overnight. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water three times, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give crude **17** as a colorless solid. We continued to the next reaction step.

3-(*tert*-Butyl)-9-methyl-6,7-dihydro-5H-benzo[7]annulen-8-yl trifluoromethanesulfonate (**18**)

Following a similar procedure used for the synthesis of **4** from **17** (0.57 g), chromatography over silica gel, eluting with 6/1 (v/v) hexane/ethyl acetate, gave crude **18** as colorless oil. Yield: 78%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.1, 2.0 Hz, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 2.1 Hz, 1H), 2.68 (t, J = 6.7 Hz, 2H), 2.29-2.24 (m, 4H), 2.15 (s, 3H), 1.33 (s, 9H) (**Figure S69**)

1,4-Bis(3-(*tert*-butyl)-9-methyl-6,7-dihydro-5H-benzo[7]annulen-8-yl)benzene (^{t}**BuDBαMDB[7]**)

Following a similar procedure used for the synthesis of **DBDB[6]** from **18** (0.68 g, 1,9 mmol) refluxed at 60°C for 2 hours, chromatography over silica gel, eluting with 6/1 (v/v) hexane/dichloromethane, recrystallization from 3/1 (v/v) hexane/dichloromethane, and purifying by recycling HPLC gave ***t*BuDBαMDB[7]** as a colorless solid. Yield: 5.7%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 4H), 7.28 (s, 4H), 7.22 (s, 2H), 2.70 (t, J = 6.7 Hz, 4H), 2.20 (s, 8H), 2.08 (s, 6H), 1.36 (s, 18H) (**Figure S70**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.4, 142.1, 140.6, 139.9, 137.6, 131.8, 128.3, 126.2, 125.5, 123.0, 34.8, 34.6, 32.9, 32.6, 31.5, 20.0 (**Figure S71**); HRMS (FAB) Calcd for $C_{38}H_{46}$: 502.3600, Found 502.3603 (**Figure S77**).

4. Photophysical properties

(1) Absorption and fluorescence spectra in THF and in the solid states

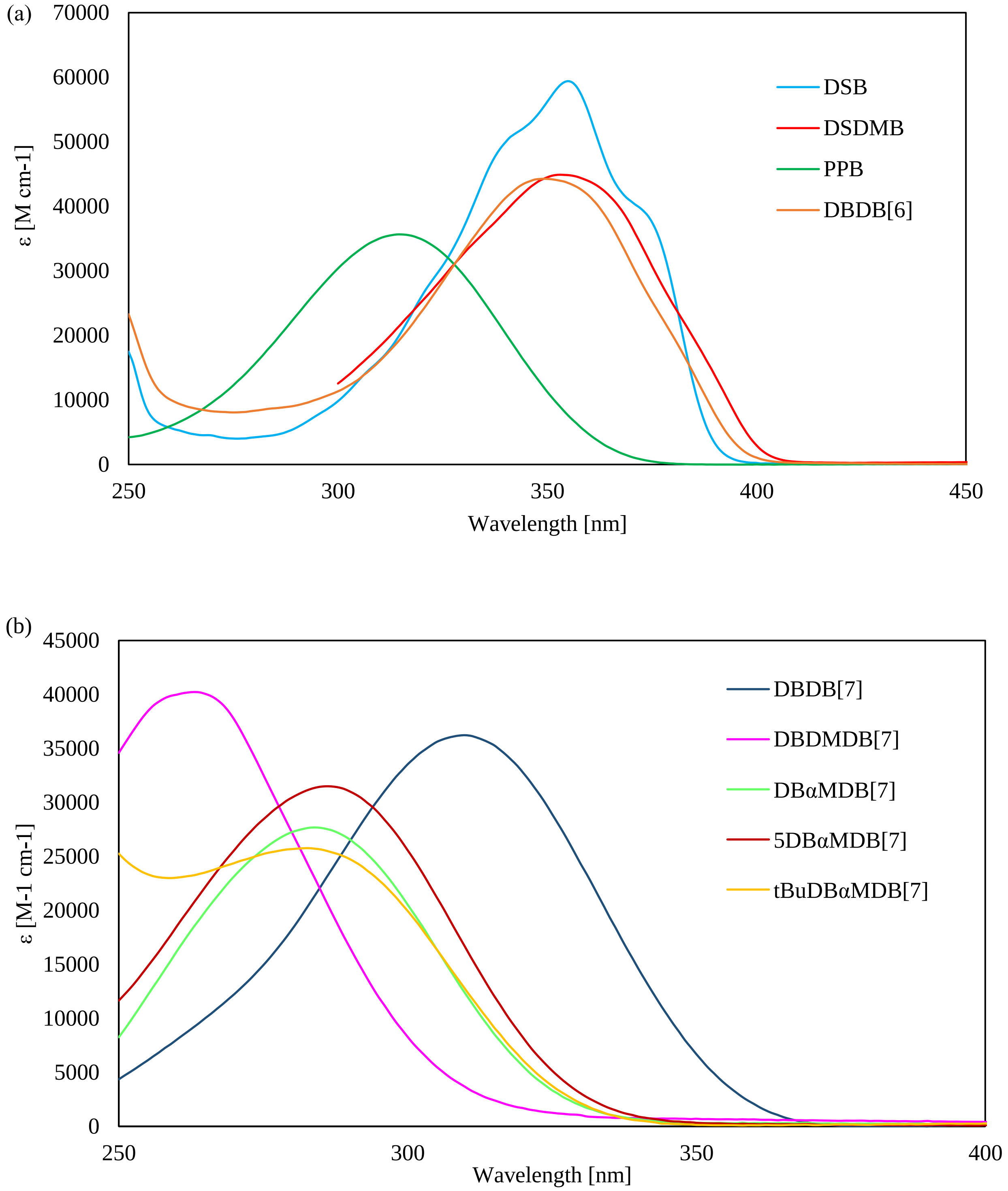


Figure S1. Absorption spectra of (a) **DSB**s (b) **DBDB[7]**s in THF.

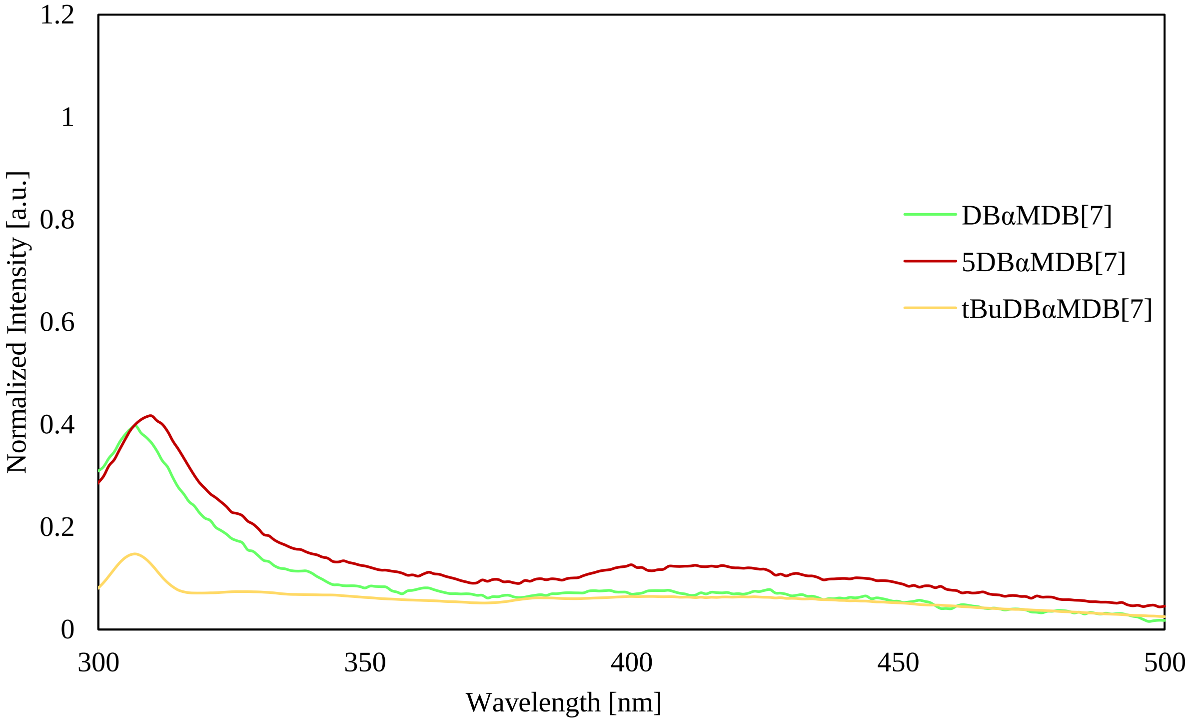
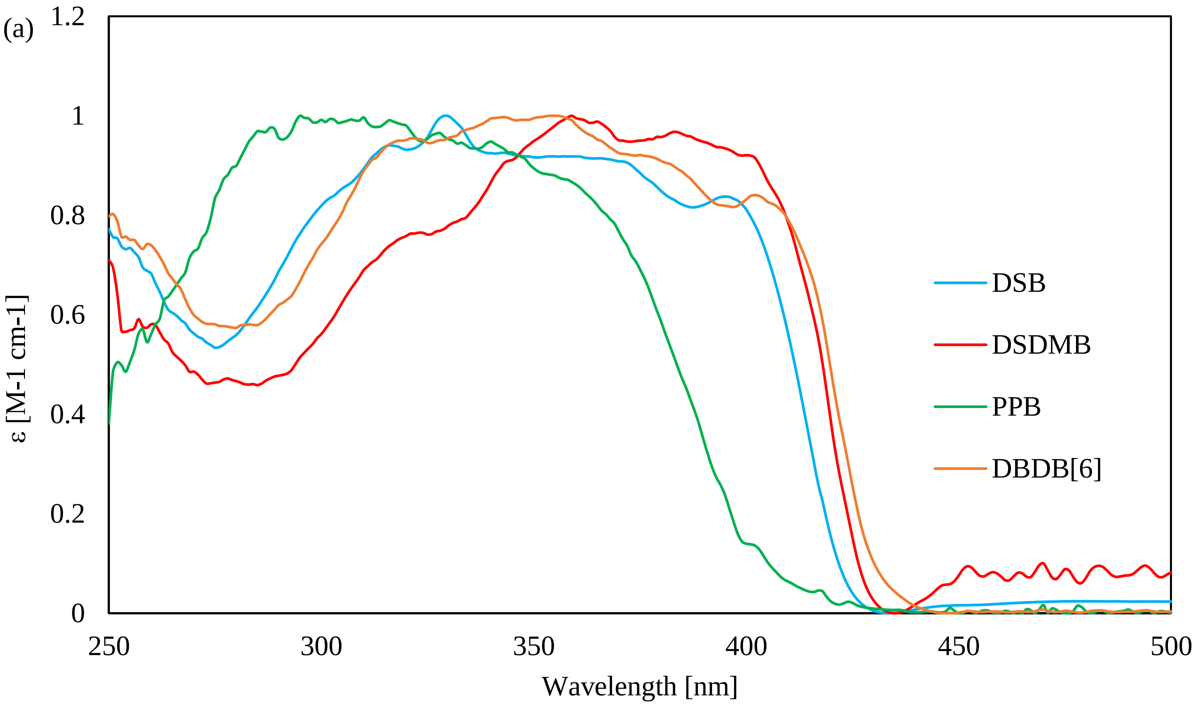


Figure S2. Fluorescence spectra of **DBαMDB[7]**s in THF (excitation wavelength of each compound is λ_{abs}). Small peaks around 310 nm were assigned to Raman scattering.



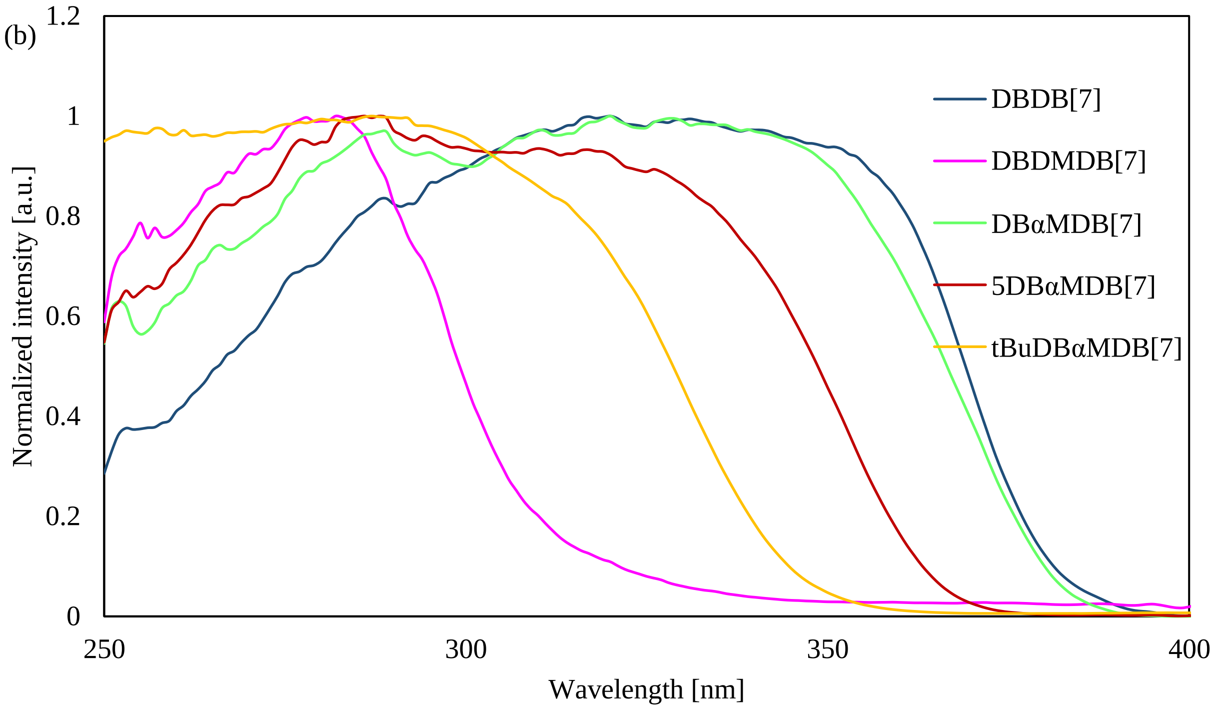


Figure S3. Diffuse-reflectance spectra of (a) **DSB**s (b) **DBDB[7]**s dispersed on NaBr powder.

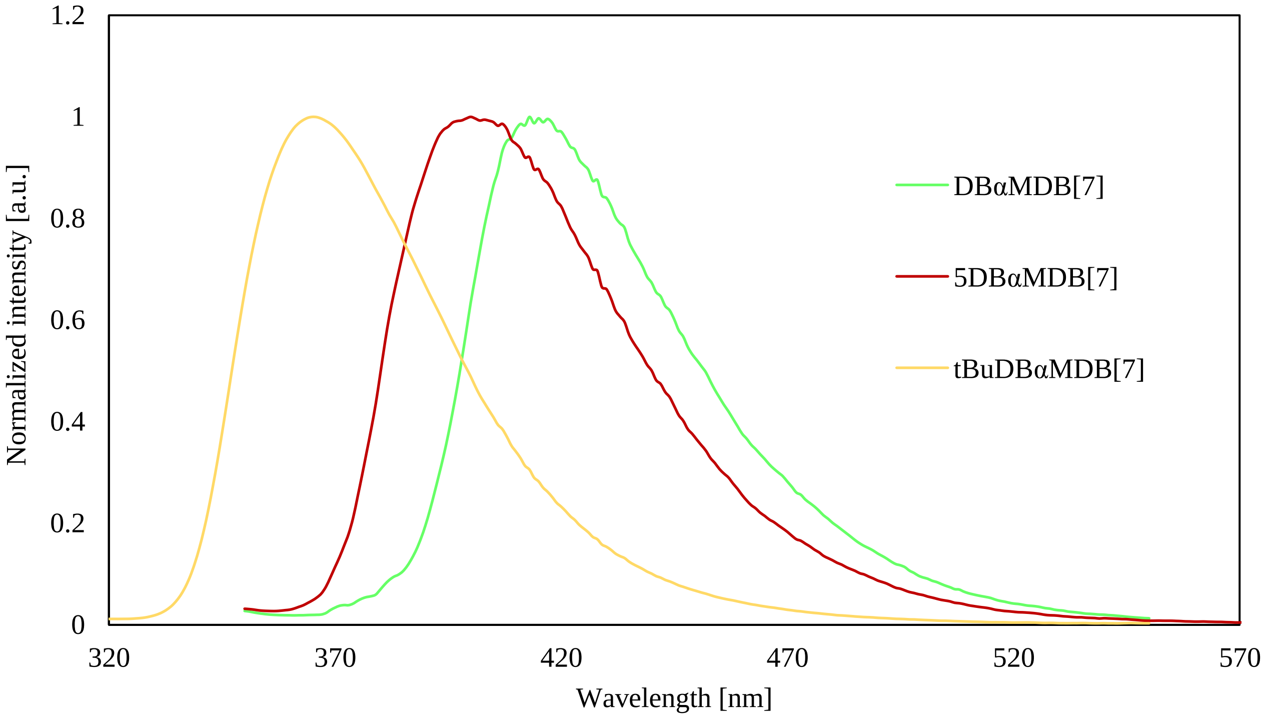


Figure S4. Fluorescence spectra of **DBαMDB[7]**s in the solid states (excitation wavelength of each compounds is λ_{abs}).

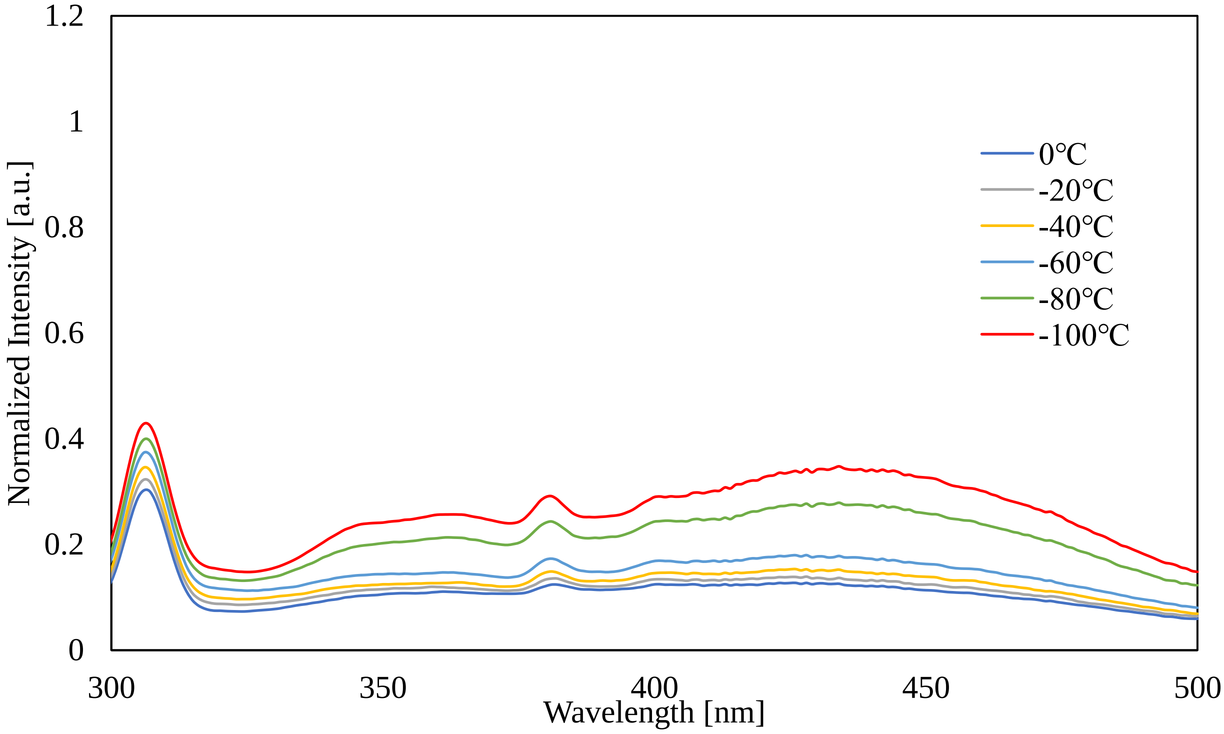


Figure S5. Fluorescence spectra of **DBαMDB[7]** in THF from 0°C to -100°C at 1.0 × 10^{-5} M (excitation wavelength is 284 nm). Small peaks around 310 nm were assigned to Raman scattering.

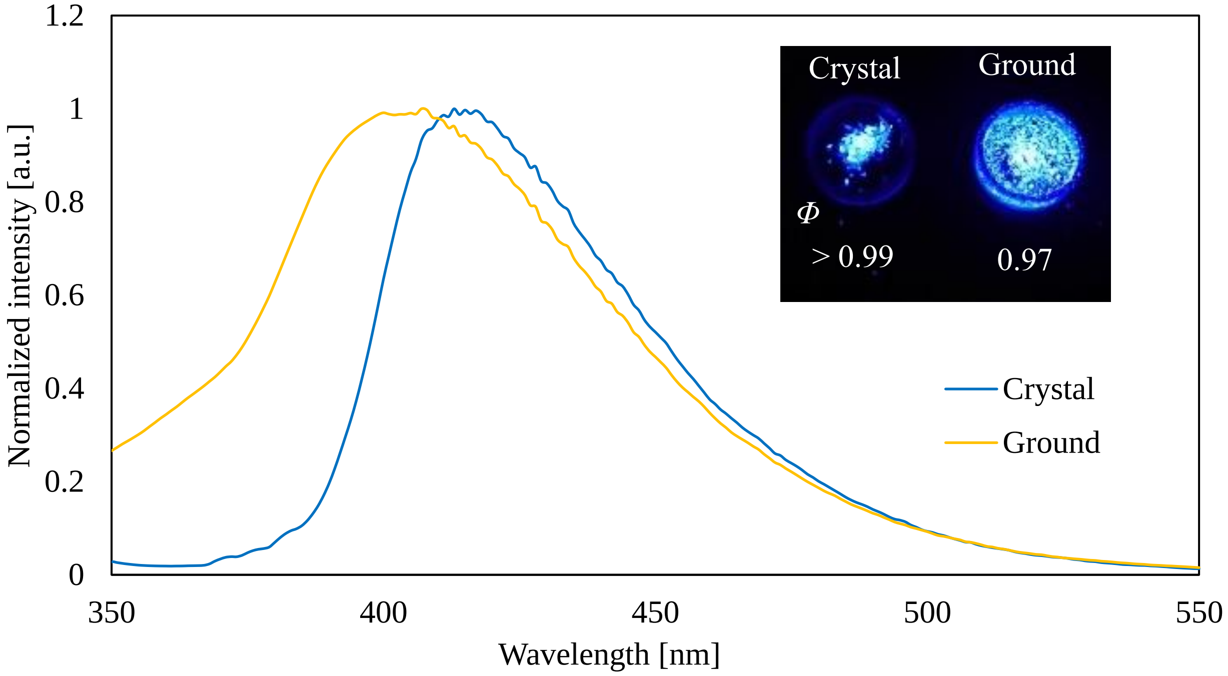


Figure S6. Fluorescence spectra (excitation at 330 nm) and photographs of crystal-**DBαMDB[7]** and ground- **DBαMDB[7]** (irradiation with 365 nm UV light).

(2) Lifetimes

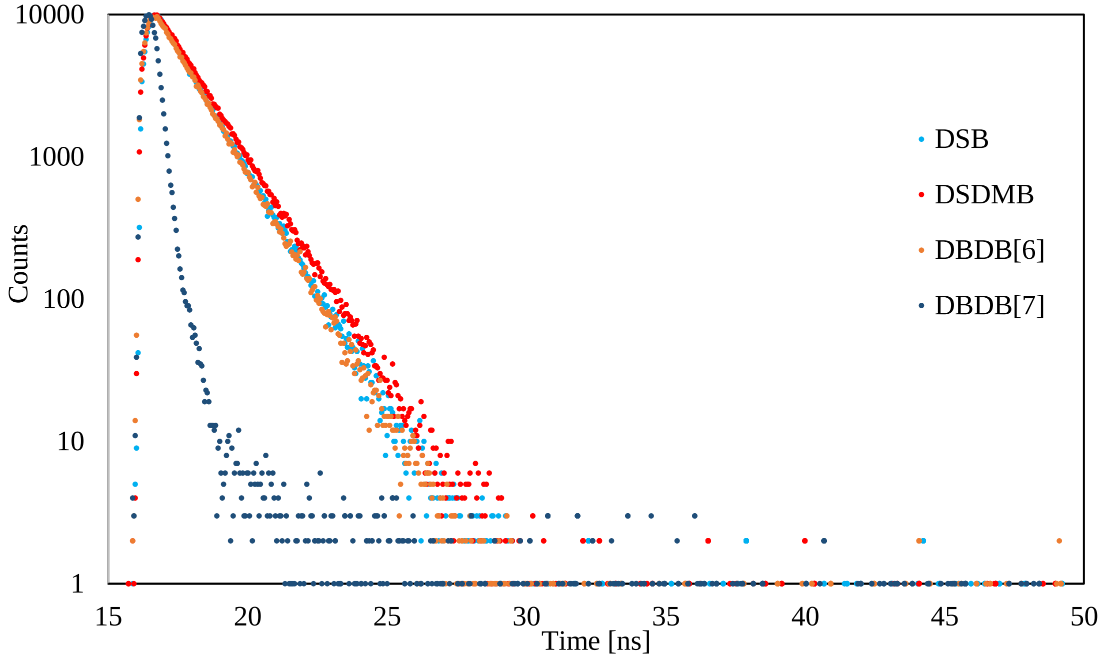


Figure S7. Time resolved fluorescence decay of **DSB**, **DSDMB**, **DBDB[6]**, and **DBDB[7]** in THF obtained on excitation at 379 nm and probing at the maxima of the fluorescence bands of each compounds, cutting wavelengths below 400 nm.

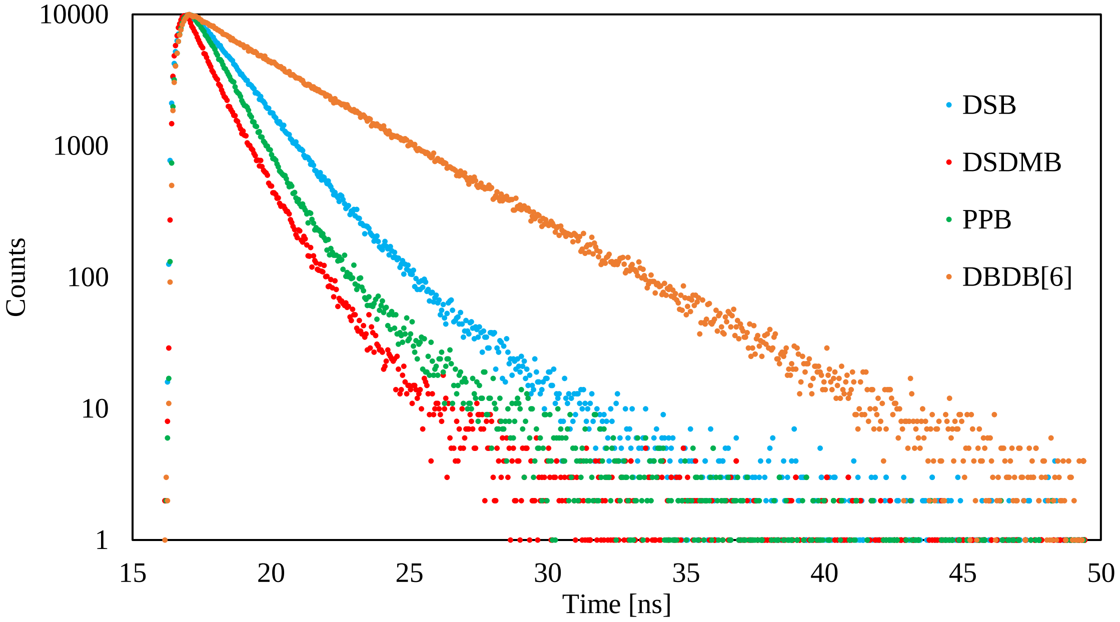


Figure S8. Time resolved fluorescence decay of **DSB**s in the solid states obtained on excitation at 379 nm and probing at the maxima of the fluorescence bands of each compounds, cutting wavelengths below 425 nm.

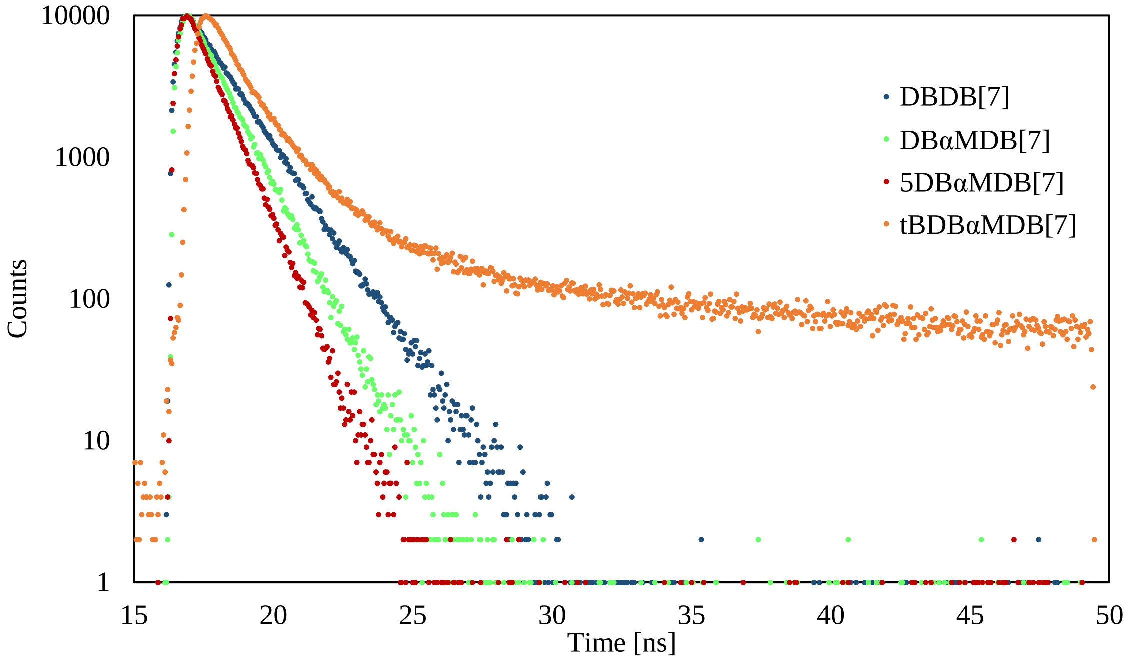


Figure S9. Time-resolved fluorescence decay of **DBDB[7]** and **DBαMDB[7]** in the solid states obtained on excitation at **DBDB[7]**, **DBαMDB[7]**, and **5DBαMDB[7]**: 379 nm and **^{t}BuDBαMDB[7]**: 269 nm, and probing at **DBDB[7]**, **5DBαMDB[7]**, and **^{t}BuDBαMDB[7]**: 410 nm and **DBαMDB[7]**: 413 nm, cutting wavelengths below 400 nm.

(3) Photophysical properties of aggregated states

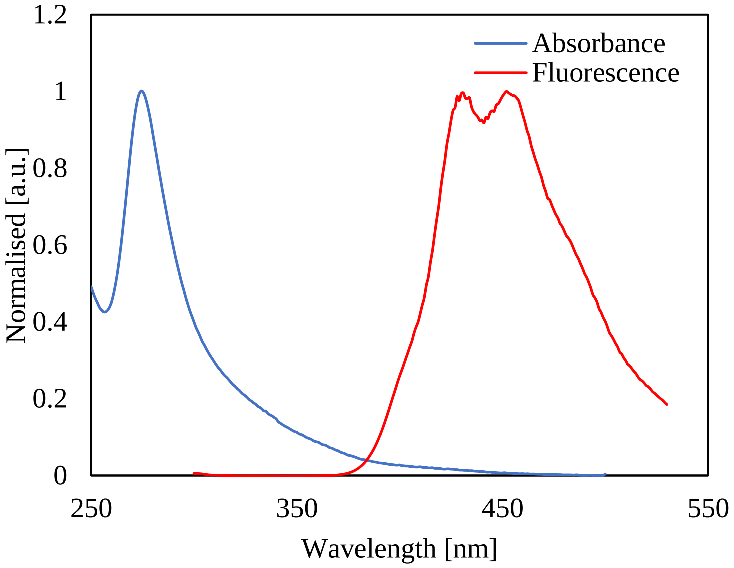


Figure S10. Absorption and fluorescence spectra of **PPB** in 2/8 (v/v) THF/water solution at 1.0× 10^{-5} M.

Table S1. Photophisical propertis of **DBDB[7]** in THF/water mixed solvent at 1.0×10^{-5} M.

Water Fraction (vol%)	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
λ_{abs} [nm]	321	320	320	320	321	321	321	322	307	320
ε [M cm^{-1}]	42000	40000	42000	41000	42000	42000	42000	12000	24000	38000
λ_{fl} [nm][a]	411	413	413	413	413	413	413	392	392	420
Φ [-]	0.108	0.106	0.092	0.103	0.104	0.103	0.099	0.572	0.689	0.446

a) Excitation wavelengths correspond to the maxima of the absorption bands.

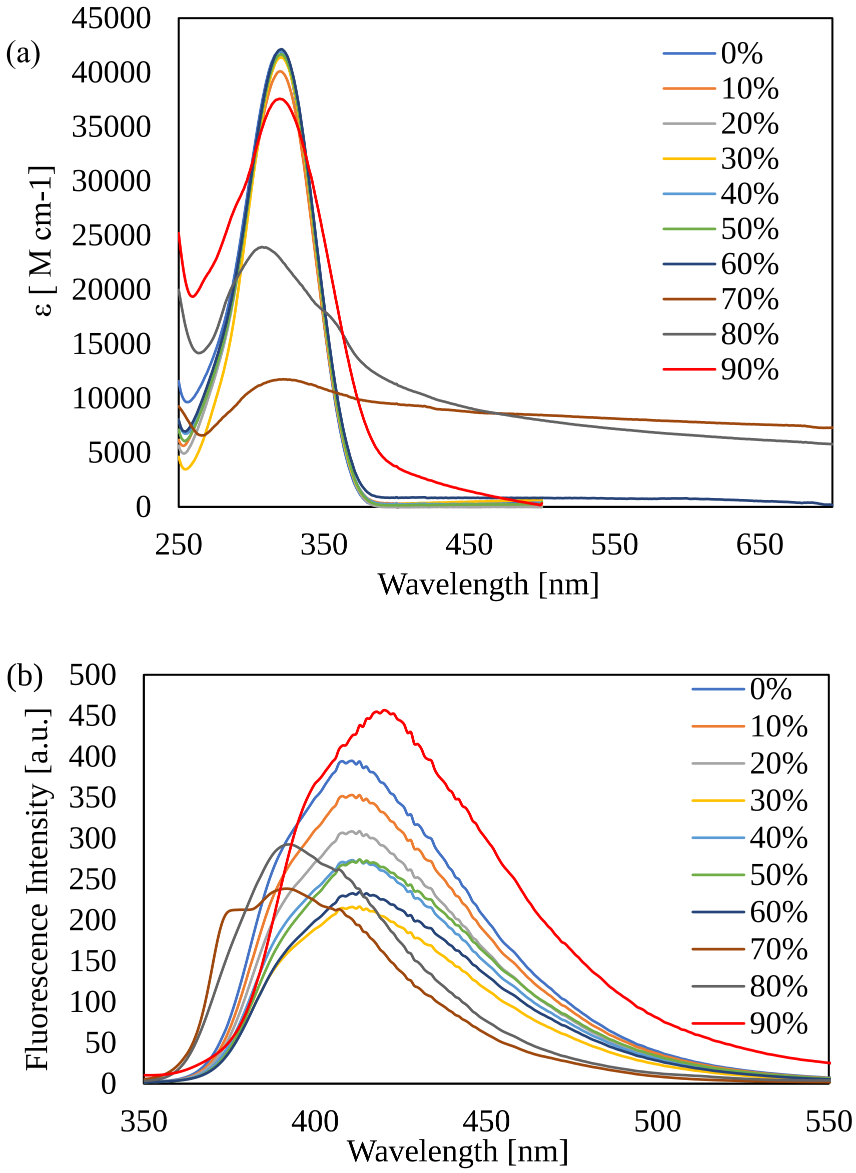
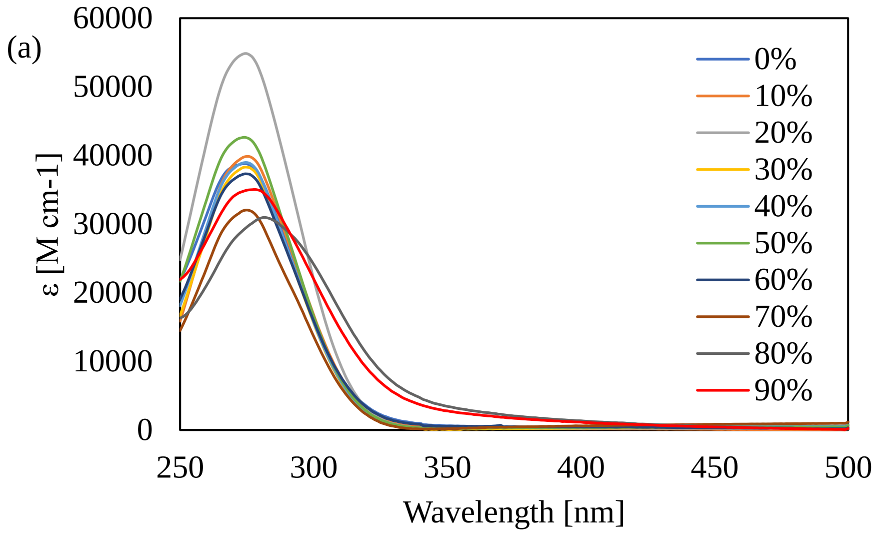


Figure S11. (a) Absorption and (b) fluorescence spectra of **DBDB[7]** in THF/water mixed solvent at 1.0 × 10^{-5} M.

Table S2. Photophysical properties of **DBDMDB[7]** in THF/water mixed solvent at 1.0 × 10^{-5} M.

Water Fraction (vol%)	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
λ_{abs} [nm]	274	275	275	275	275	274	275	275	282	278
ε [M cm^{-1}]	39000	40000	55000	38000	39000	43000	37000	32000	31000	35000
λ_{fl} [nm][a]	394	397	394	396	396	397	394	385	398	394
Φ [-]	0014	0.009	0.007	0.013	0.009	0.015	0.014	0.021	0.023	0.062

a) Excitation wavelengths correspond to the maxima of the absorption bands.



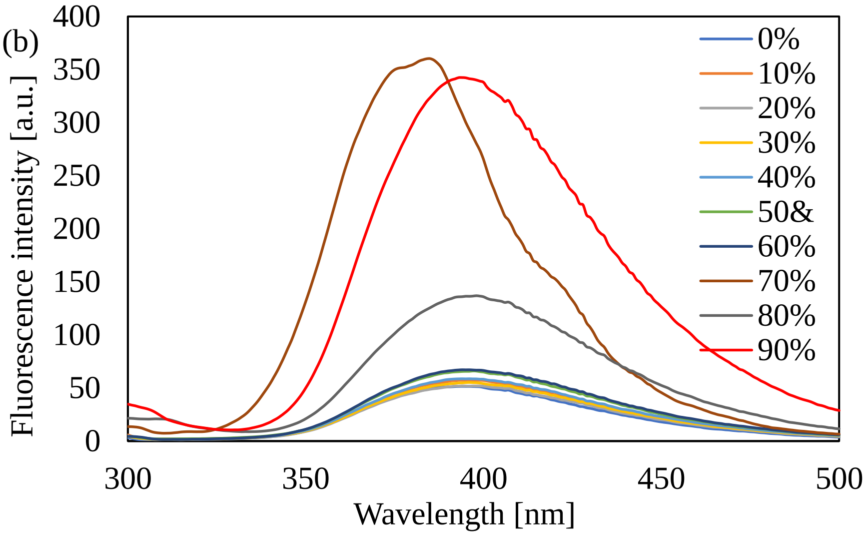


Figure S12. (a) Absorption and (b) fluorescence spectra of **DBDMDB[7]** in THF/water mixed solvent at 1.0 × 10^{-5} M.

Table S3. Photophysical properties of **DBαMDB[7]**in THF/water mixed solvent at 1.0 × 10^{-5} M.

Water Fraction (vol%)	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
λ_{abs} [nm]	284	283	284	285	283	284	284	286	295	286
ε [M cm^{-1}]	30000	30000	29000	27000	30000	30000	30000	25000	24000	26000
λ_{fl} [nm]^{a}	-	-	-	-	-	-	-	359	428	423
Φ [-]^{a}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	0.04	0.12

a) Excitation wavelengths correspond to the maxima of the absorption bands.

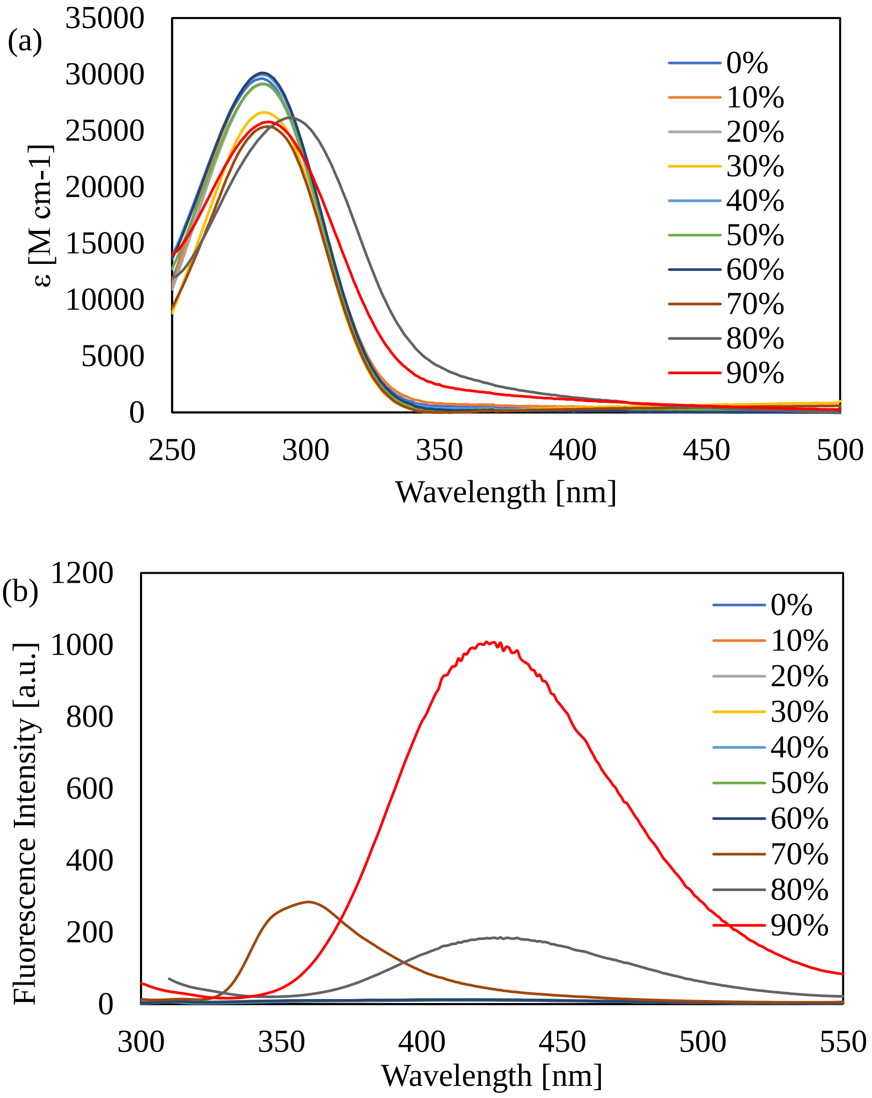


Figure S13. (a) Absorption and (b) fluorescence spectra of **DBαMDB[7]** in THF/water mixed solvent at 1.0×10^{-5} M.

(4) Solvatchromism of **DBDB[7]**

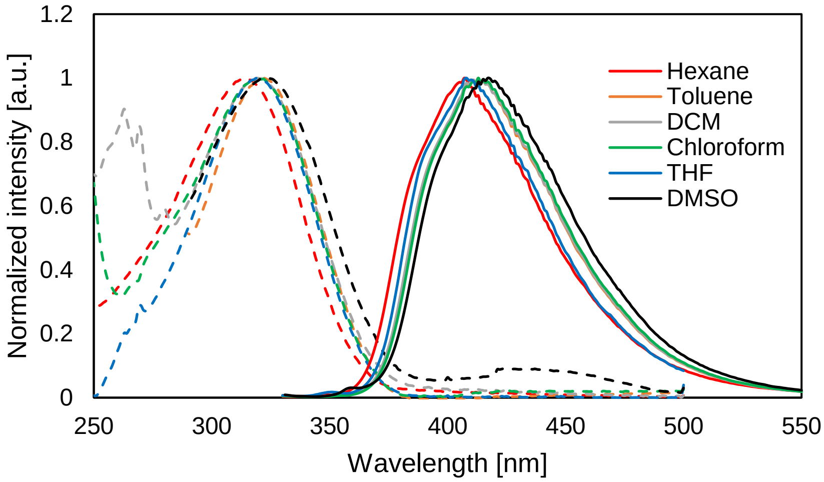


Figure S14. Absorption (dased lines) and fluorescence (solid lines) spectra of **DBDB[7]** in hexane, toluene, dichloromethane (DCM), chloroform, THF, and dimethyl sulfoxide (DMSO) with ODs of approximately 0.1.

Table S4. Photophysical properties of **DBDB[7]** in various solvents.

Solvent	**Hexane**	**Toluene**	**DCM**	**Chloroform**	**THF**	**DMSO**
λ_{abs} [nm]	315	321	320	320	320	324
λ_{fl} [nm]^{a}	407	413	413	413	408	417
Φ [-]^{a}	0.08	0.11	0.09	0.11	0.11	0.14

a) Excitation wavelengths correspond to the maxima of the absorption bands.

(5) Photophysical properties of PMMA cast films of **DBDB[7]s**.

Methods of making cast films.

PMMA (*Mw* = 100,000) and **DBDB[7]s** (about 0.1 wt%) was dissolved in THF to reach a concentration of about 0.025 g/ml. The mixture was stired at room temperature for 3 hours, then ultrasonicated for 20 seconds. The mixture was dropped on a quarts plate and dried at room temperature for 2 days to give a PMMA cast film with 0.1 wt% **DBDB[7]s**.

Table S5. Photophysical properties of the PMMA cast films doped with **DBDB[7]s**.

Dopant	λ_{abs} **[nm]**	λ_{fl} **[nm]**[a]	Φ **[-]**
DBDB[7]	309	407	0.55[b]
DBDMDB[7]	272	384	0.13[c]
DBαMDB[7]	292	407	0.24[d]
5DBαMDB[7]	293	407	0.42[d]
^{t}BuDBαMDB[7]	278	408	0.48[d]

Excitation wavelengths: a) corresponds to the maxima of the absorption bands.; b) 330 nm; c) 290 nm; d) 300 nm.

λ_{fl} of the cast film of **^{t}BuDBαMDB[7]** is about 40 nm red-shifted compared to that in the solid states. Unlike in the solid state, **^{t}BuDBαMDB[7]** in PMMA cast film may adopt almost the same conformation to **DBαMDB[7]-cross**, because λ_{fl} of PMMA cast films of **DBαMDB[7]s** are very similar.

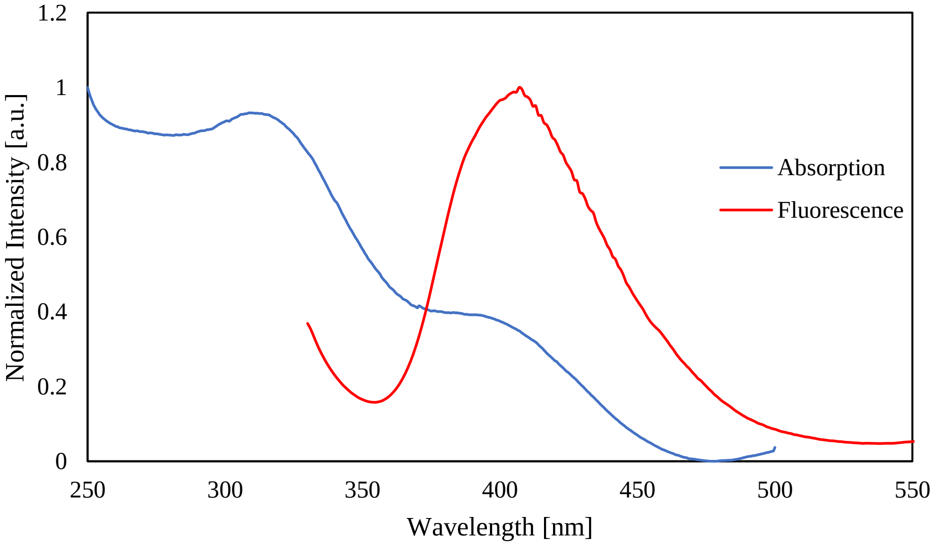


Figure S15. Absorption and fluorescence spectra of the **DBDB[7]**-doped cast film.

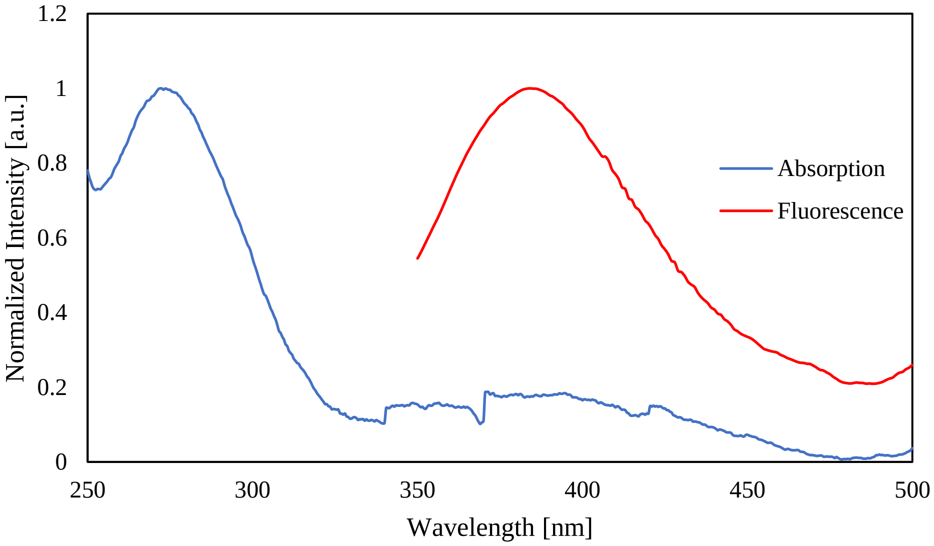


Figure S16. Absorption and fluorescence spectra of the **DBDMDB[7]**-doped cast film.

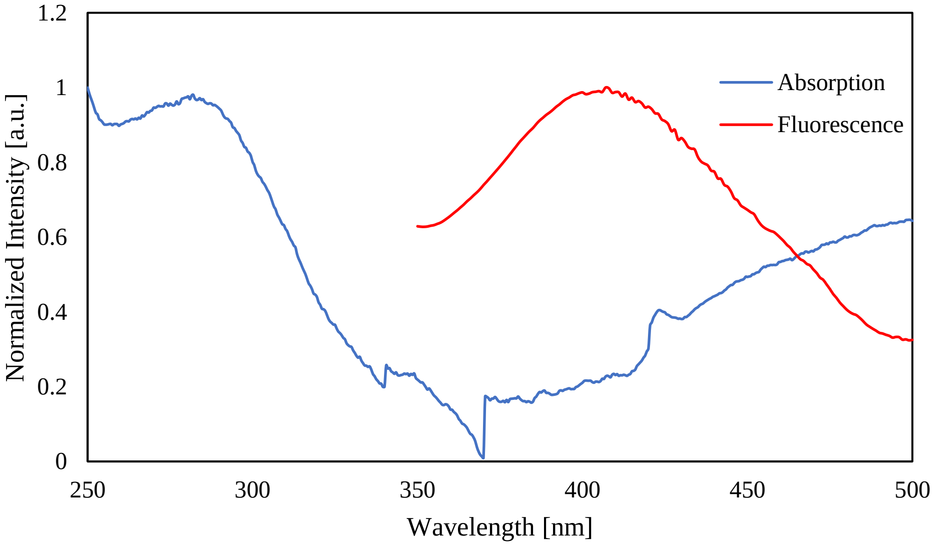


Figure S17. Absorption and fluorescence spectra of the **DBαMDB[7]**-doped cast film.

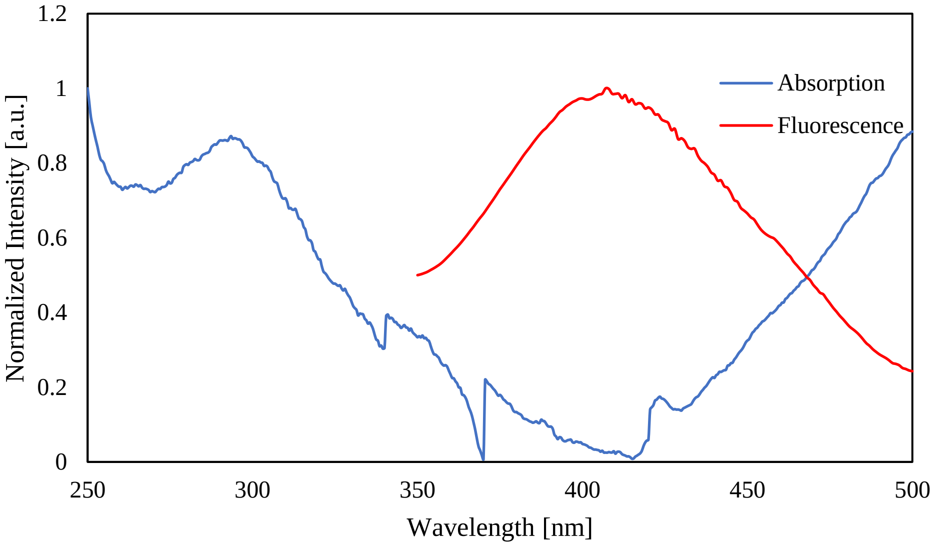


Figure S18. Absorption and fluorescence spectra of the **5DBαMDB[7]**-doped cast film.

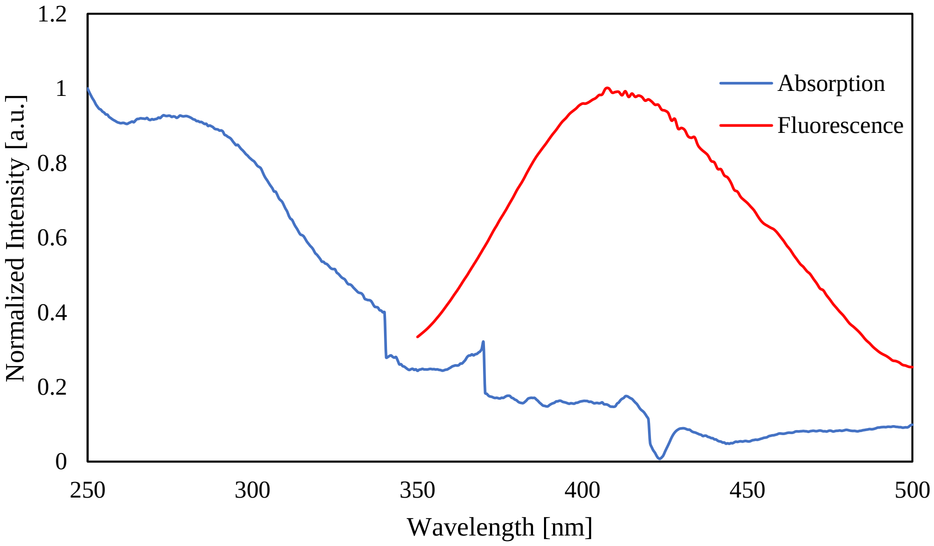


Figure S19. Absorption and fluorescence spectra of the ***ᵗ*****BuDBαMDB[7]**-doped cast film**.**

5. Physical properties

Table S6. Density and occupancy of **DSB**[12], **DSDMB**, **PPB**[4],**DBDB[7]**, **DBDMDB[7]**, **DBαMDB[7]-cross**, and **DBαMDB[7]-parallel** in the single crystal.

Entry	Density (g/cm^{-3})	Occupancy (%)
DSB	1.229	83.9
DSDMB	1.204	83.2
PPB	1.178	81.1
DBDB[7]	1.271	84.4
DBDB[7]	1.213	81.5
DBαMDB[7]-cross	1.243	83.1
DBαMDB[7]-parallel	1.210	81.0

Table S7. Melting points (T_m) of all compounds.

Entry	T_m (°C)
DSB	257.0
DSDMB	196.7
PPB	172.9
DBDB[6]	243.2
DBDB[7]	158.1
DBDMDB[7]	156.9
DBαMDB[7]	160.7
5DBαMDB[7]	125.6
^{t}BuDBαMDB[7]	311.3

6. The single-crystal x-ray structure

Although, the quality of single crystal X-ray crystallographic analysis of **DBDB[6]** is not high, we added **DBDB[6]** to the comparison of packing structures for more meaningful discussion of fluorescent property of crystallin distyrylbenzenes.

(1) Molecular structures

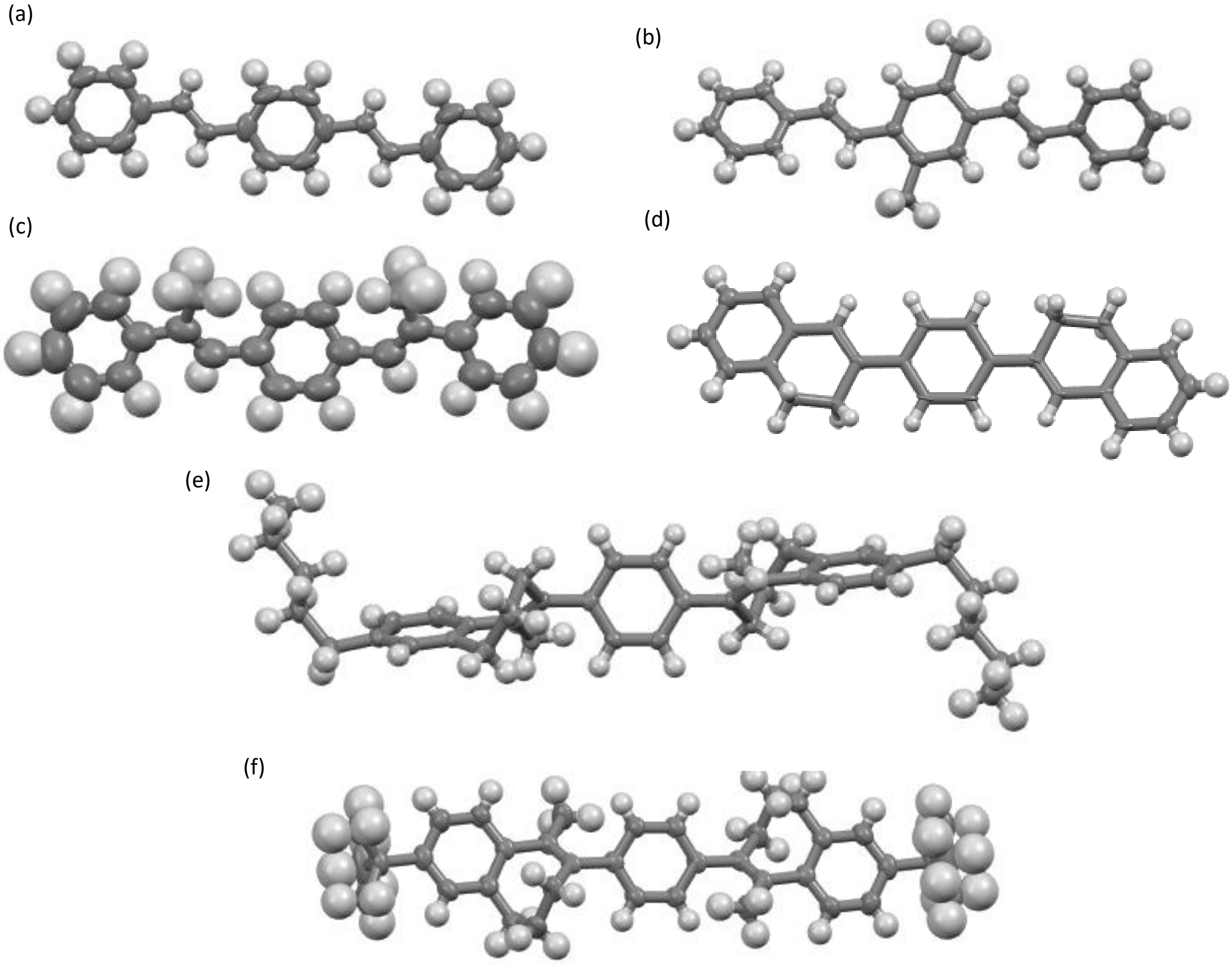


Figure S20. The front view of (a) **DSB**[12], (b) **DSDMB**, (c) **PPB**[14], (d) **DBDB[6]**, (e) **5DBαMDB[7]**, and (f) **^{t}BuDBαMDB[7]** molecule in single crystal.

(2) Single crystal X-ray

Table S8. Crystal date for **DSB**[12], **DSDMB**, **PPB**[4], **DBDB[6]**, **DBDB[7]**, and **DBDMDB[7]**.

Compound Name	**DSB**	**DSDMB**	**PPB**	**DBDB[6]**	**DBDB[7]**	**DBDMDB[7]**
Space Group	P-1	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	P-1	$P2_1/c$
Cell Lengths (Å)	**a** 5.9165	**a** 11.3650	**a** 36.813	**a** 6.2540	**a** 7.8987	**a** 16.046
	b 7.4503	**b** 7.0916	**b** 6.2947	**b** 7.5229	**b** 9.0080	**b** 8.373
	c 51.924	**c** 21.4912	**c** 7.5555	**c** 36.785	**c** 13.8356	**c** 8.128
Cell Angles (°)	**α** 88.804	**α** 90	**α** 90	**α** 90	**α** 99.206	**α** 90
	β 89.643	**β** 98.708	**β** 90	**β** 92.181	**β** 102.460	**β** 101.706
	γ 89.945	γ 90	γ 90	γ 90	γ 90.999	γ 90
Cell Volume (Å^3)	2288.25	1712.14	1750.81	1729.41	947.477	1069.31
Z	6	4	4	4	2	2

Table S9. Crystal date for **DBαMDB[7]-cross**, **DBαMDB[7]-parallel**, **5DBαMDB[7]**, and **^{t}BuDBαMDB[7]**.

Compound Name	**DBαMDB[7]-cross**	**DBαMDB[7]-parallel**	**5DBαMDB[7]**	**^{t}BuDBαMDB[7]**
Space Group	$P2_1/c$	$P2_1/c$	P-1	P-1
Cell Lengths (Å)	**a** 10.2319	**a** 8.3896	**a** 8.149	**a** 5.8767
	b 11.0510	**b** 8.4692	**b** 9.767	**b** 6.1160
	c 9.6513	**c** 15.4856	**c** 10.899	**c** 20.3049
Cell Angles (°)	**α** 90	**α** 90	**α** 107.924	**α** 93.452
	β 107.110	**β** 103.274	**β** 105.686	**β** 91.590
	γ 90	γ 90	γ 102.185	γ 93.560
Cell Volume (Å^3)	1043	1070.9	752.521	726.704
Z	5	5	1	2

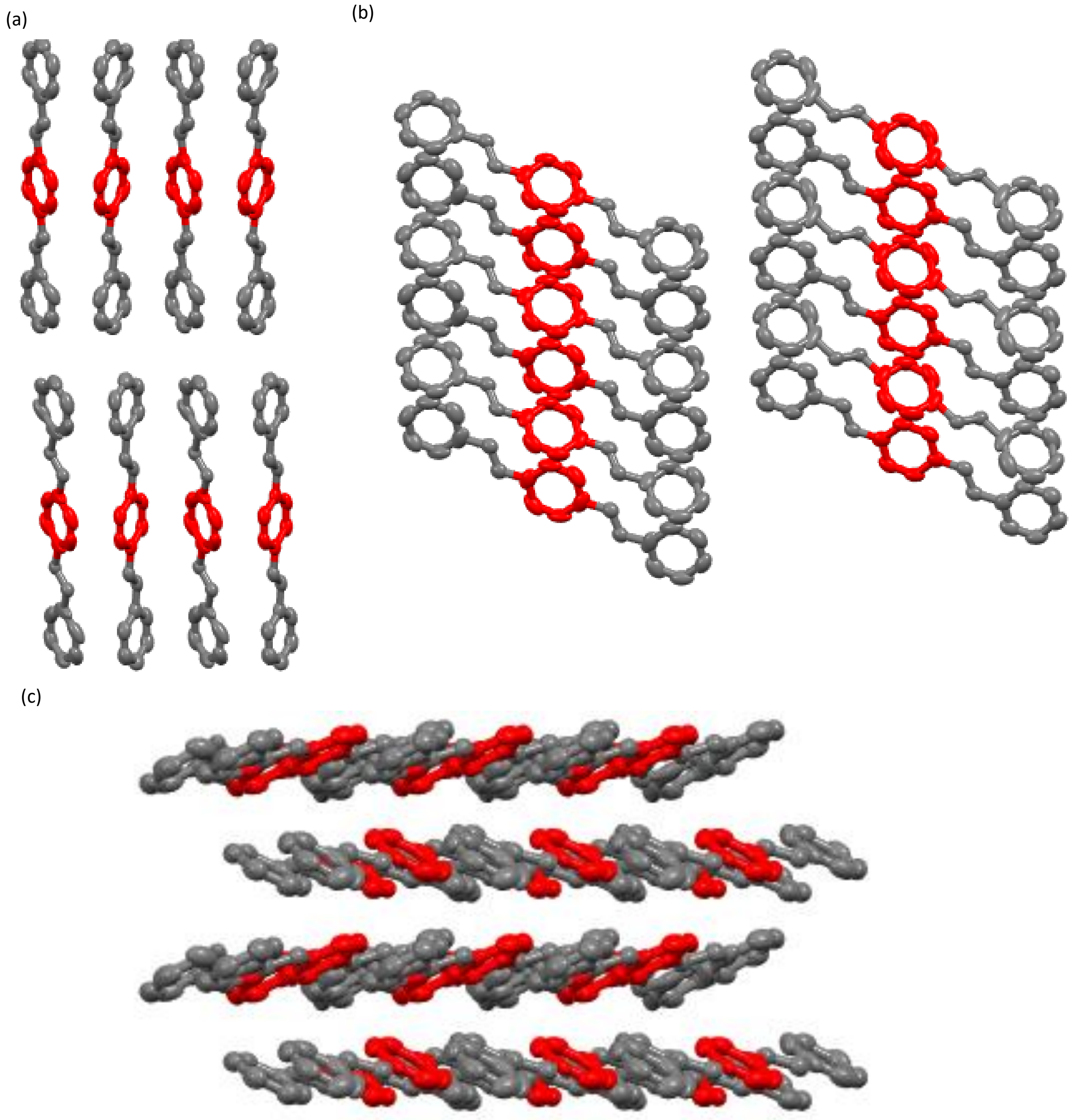


Figure S21. Projection of the structure of **DSB**[12] viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

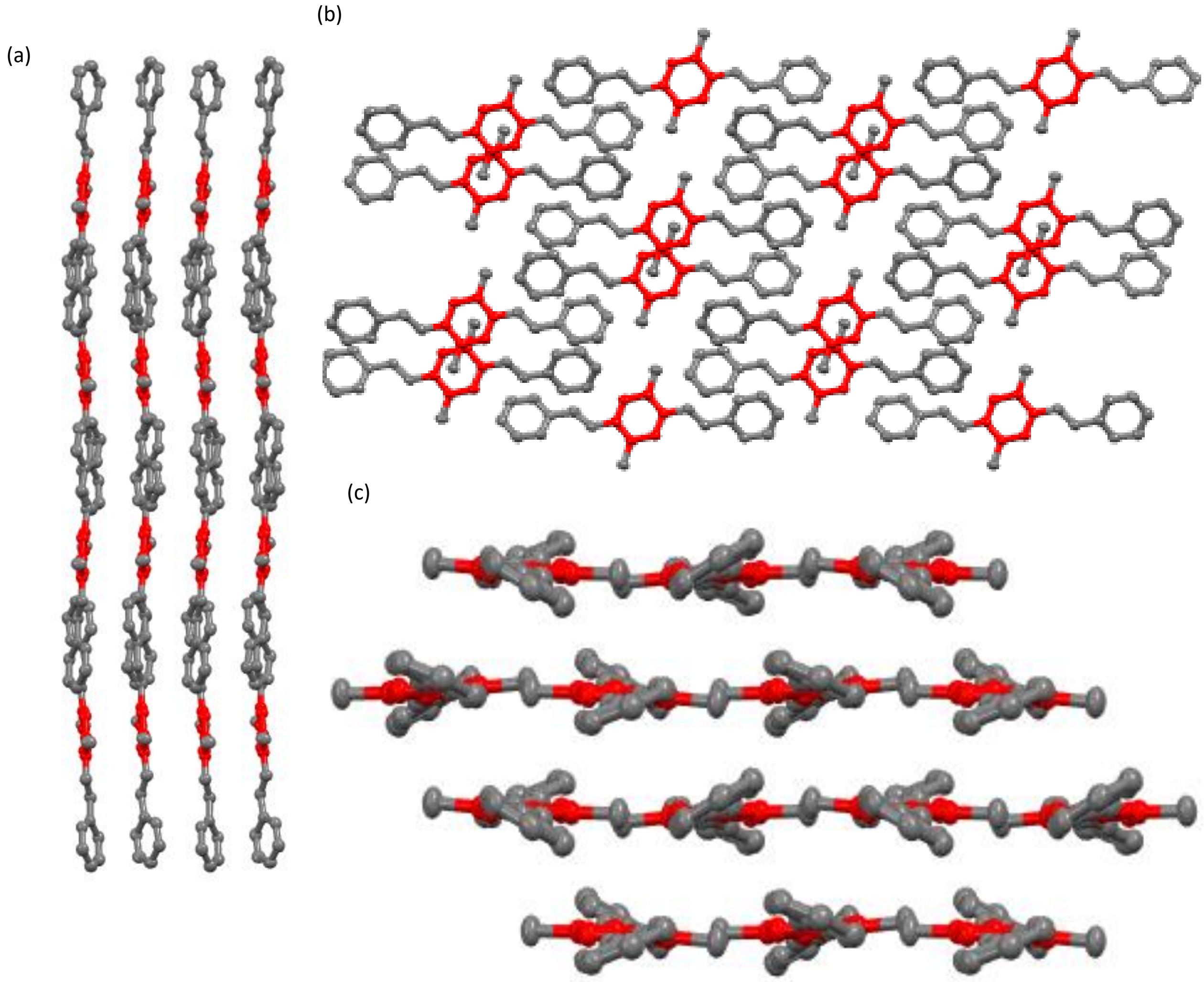


Figure S22. Projection of the structure of **DSDMB** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

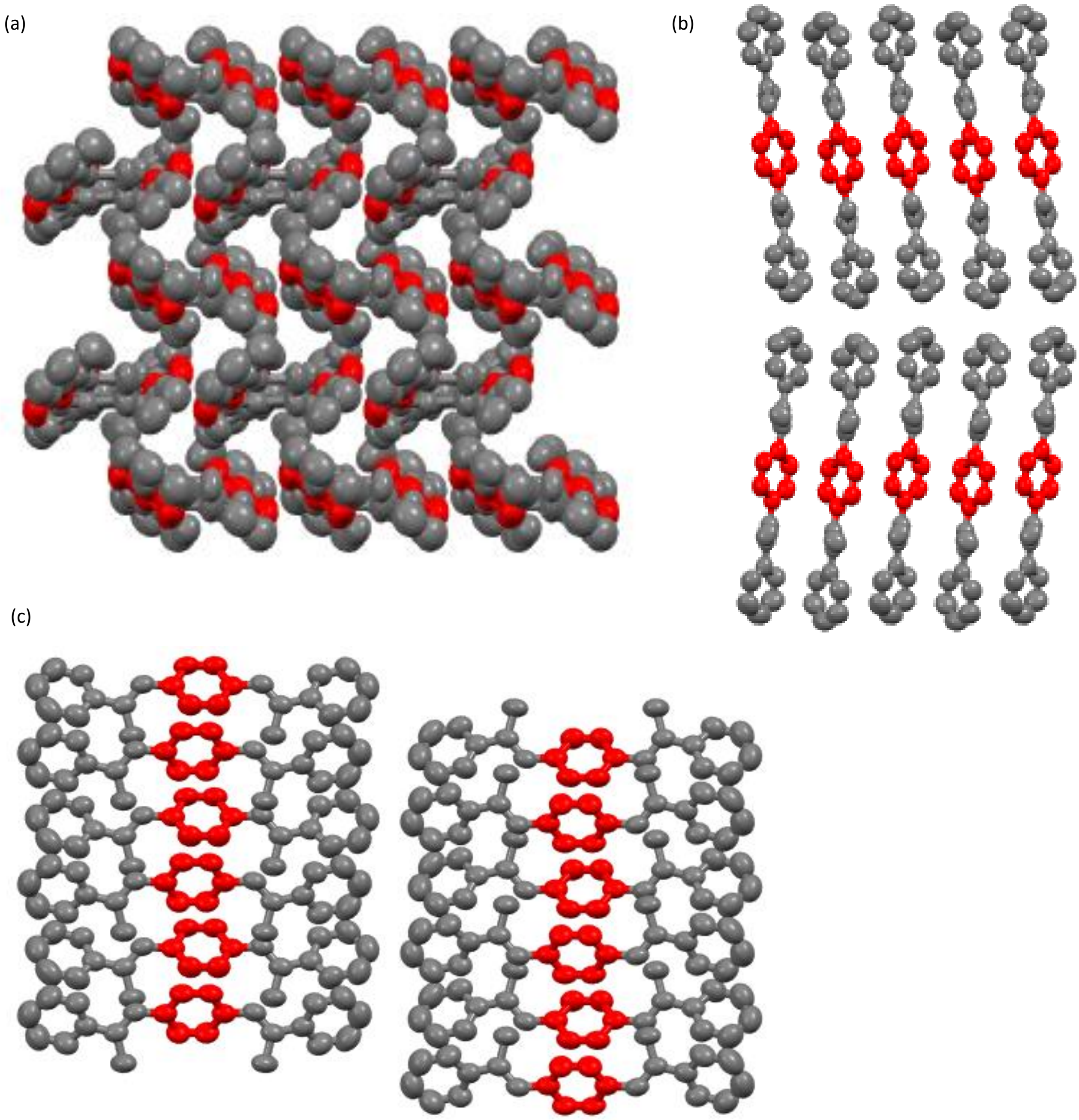


Figure S23. Projection of the structure of **PPB**[4] viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

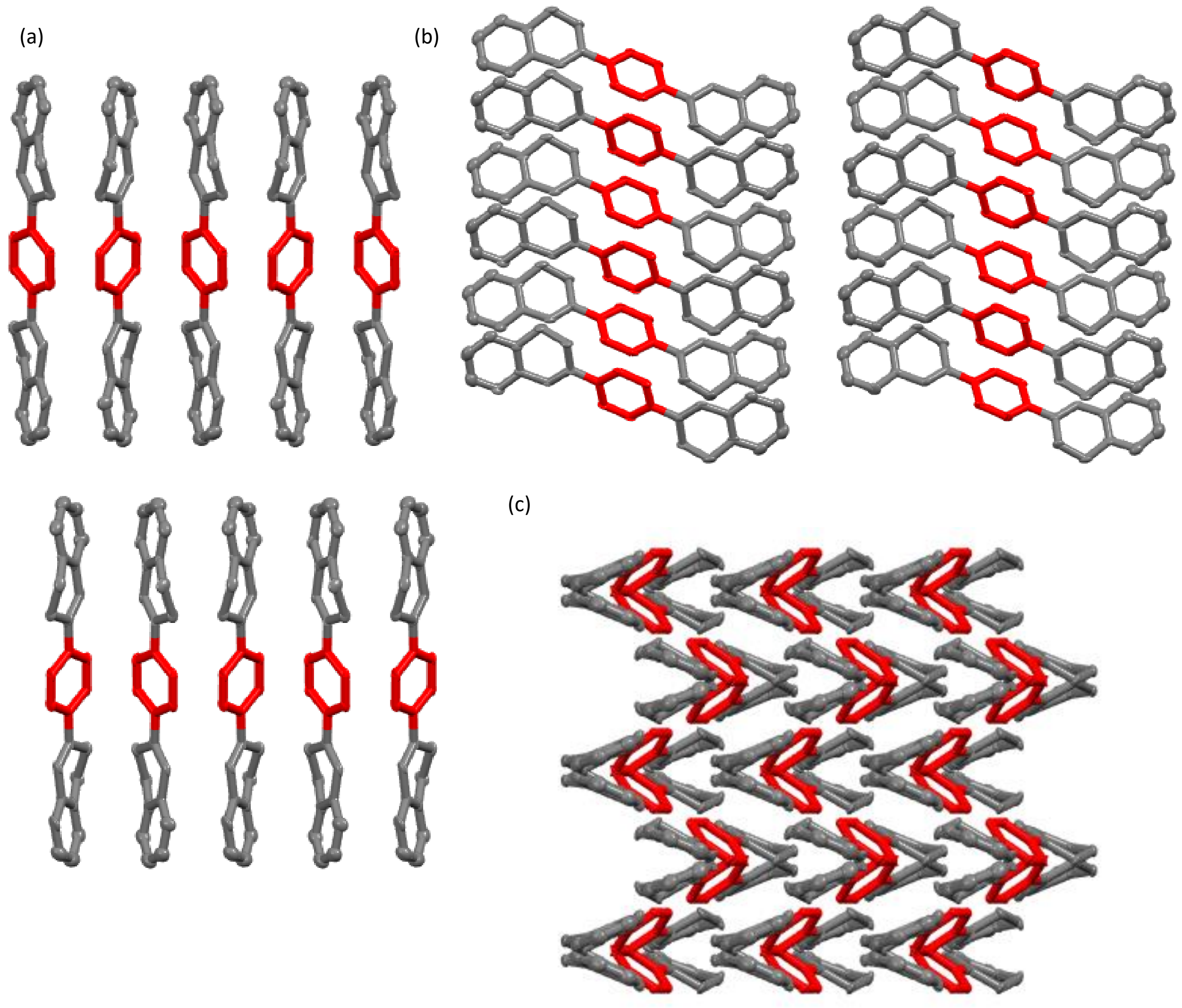


Figure S24. Projection of the structure of **DBDB[6]** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

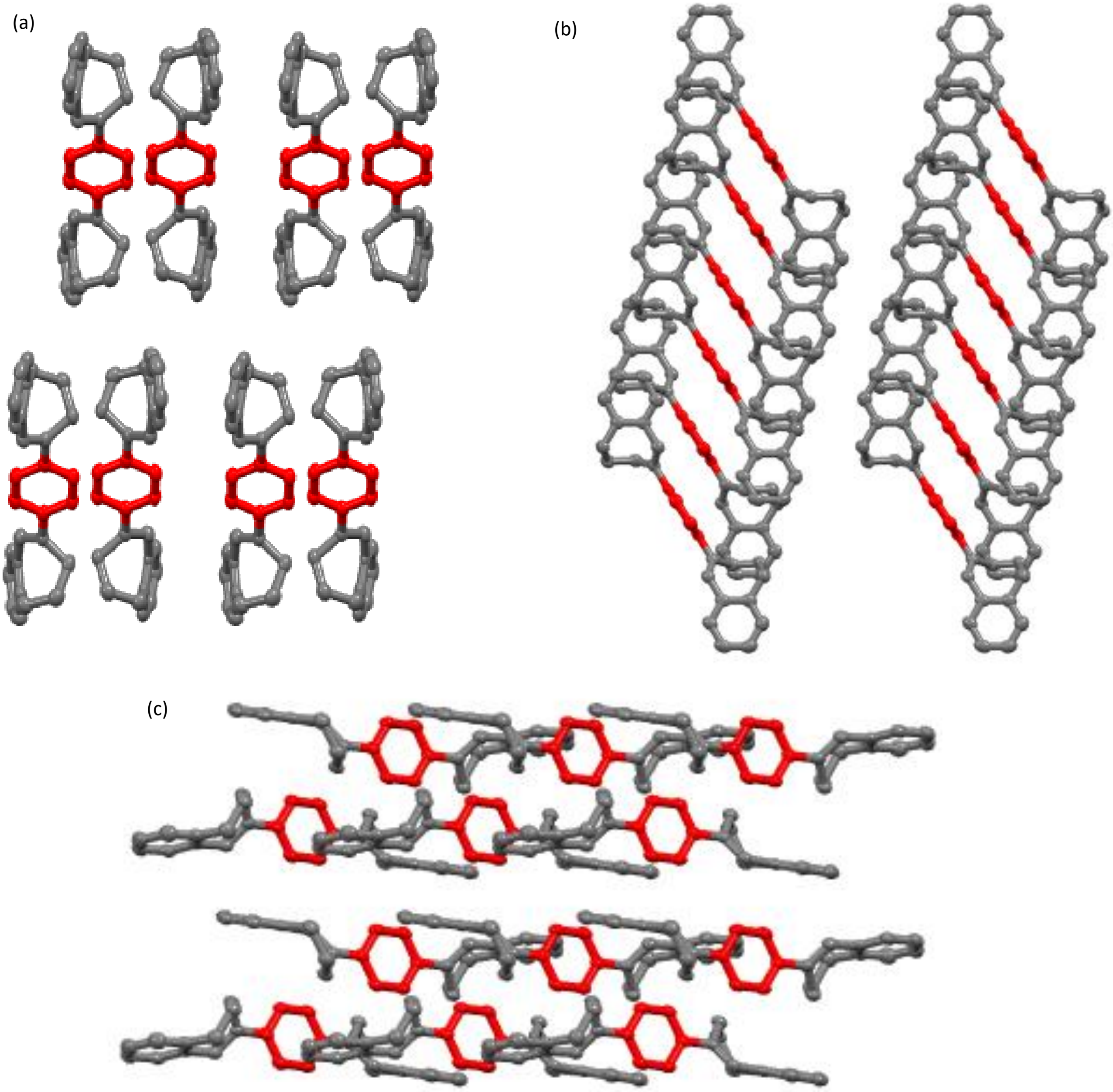


Figure S25. Projection of the structure of **DBDB[7]** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

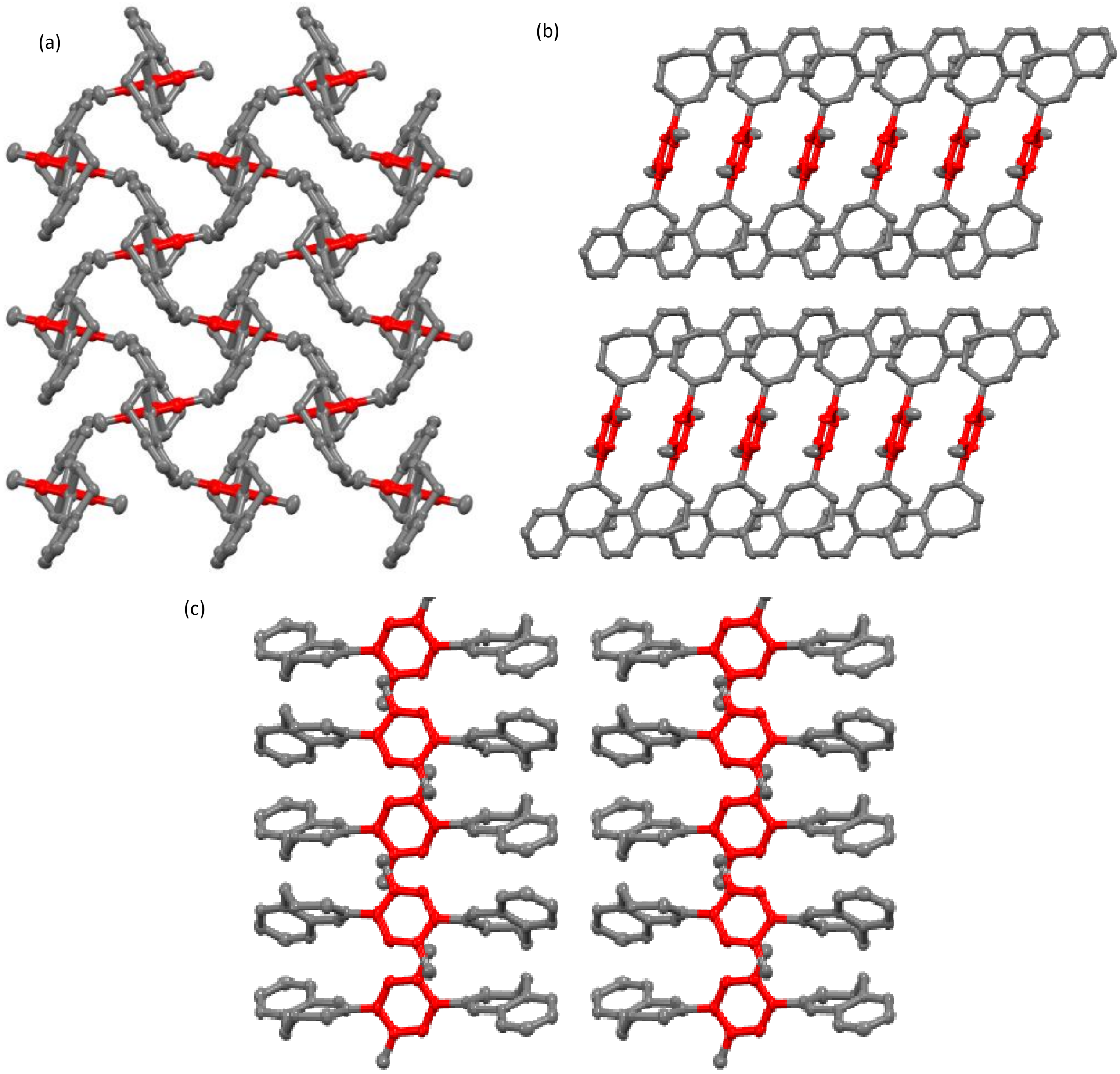


Figure S26. Projection of the structure of **DBDMDB[7]** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

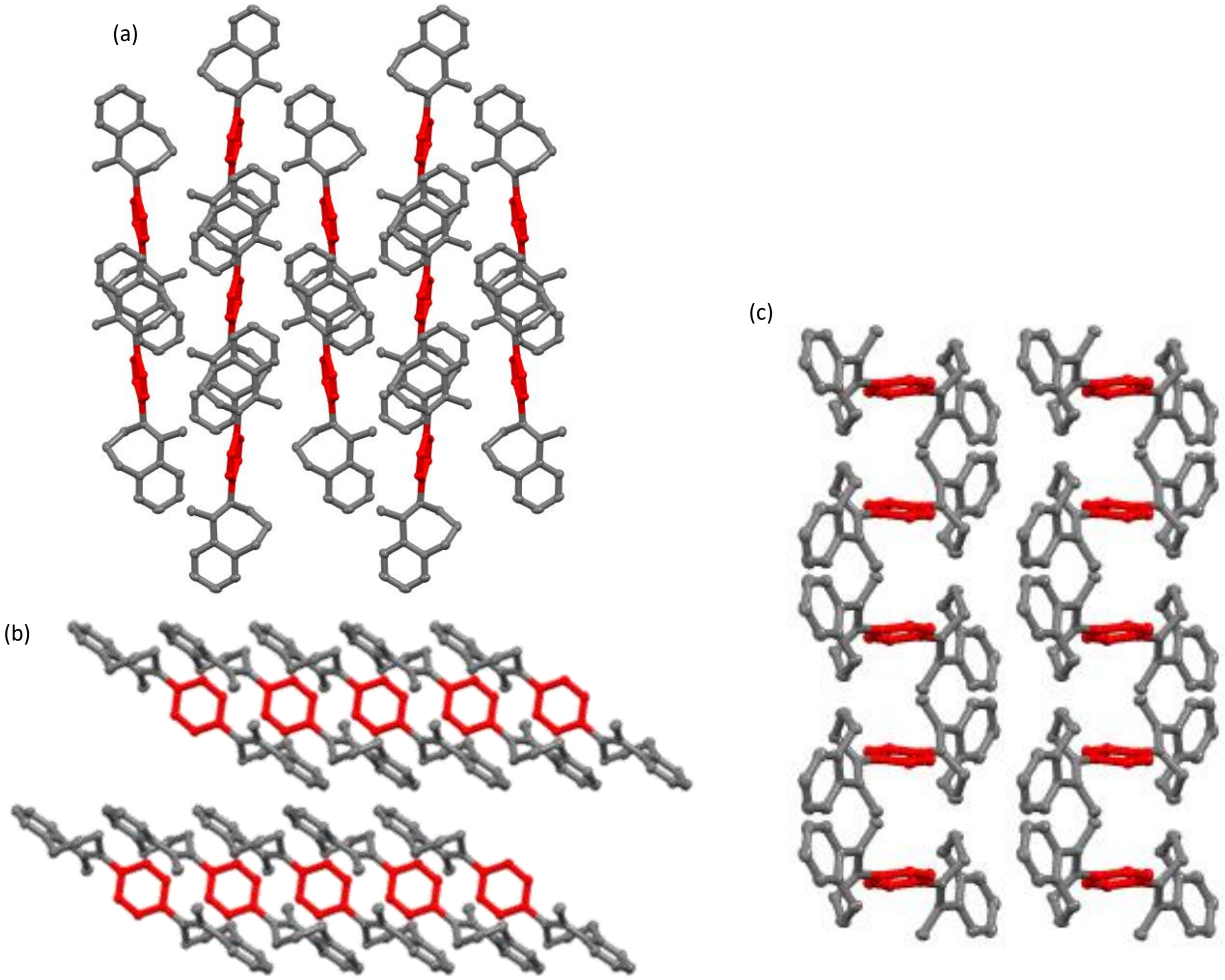


Figure S27. Projection of the structure of **DBαMDB[7]-cross** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

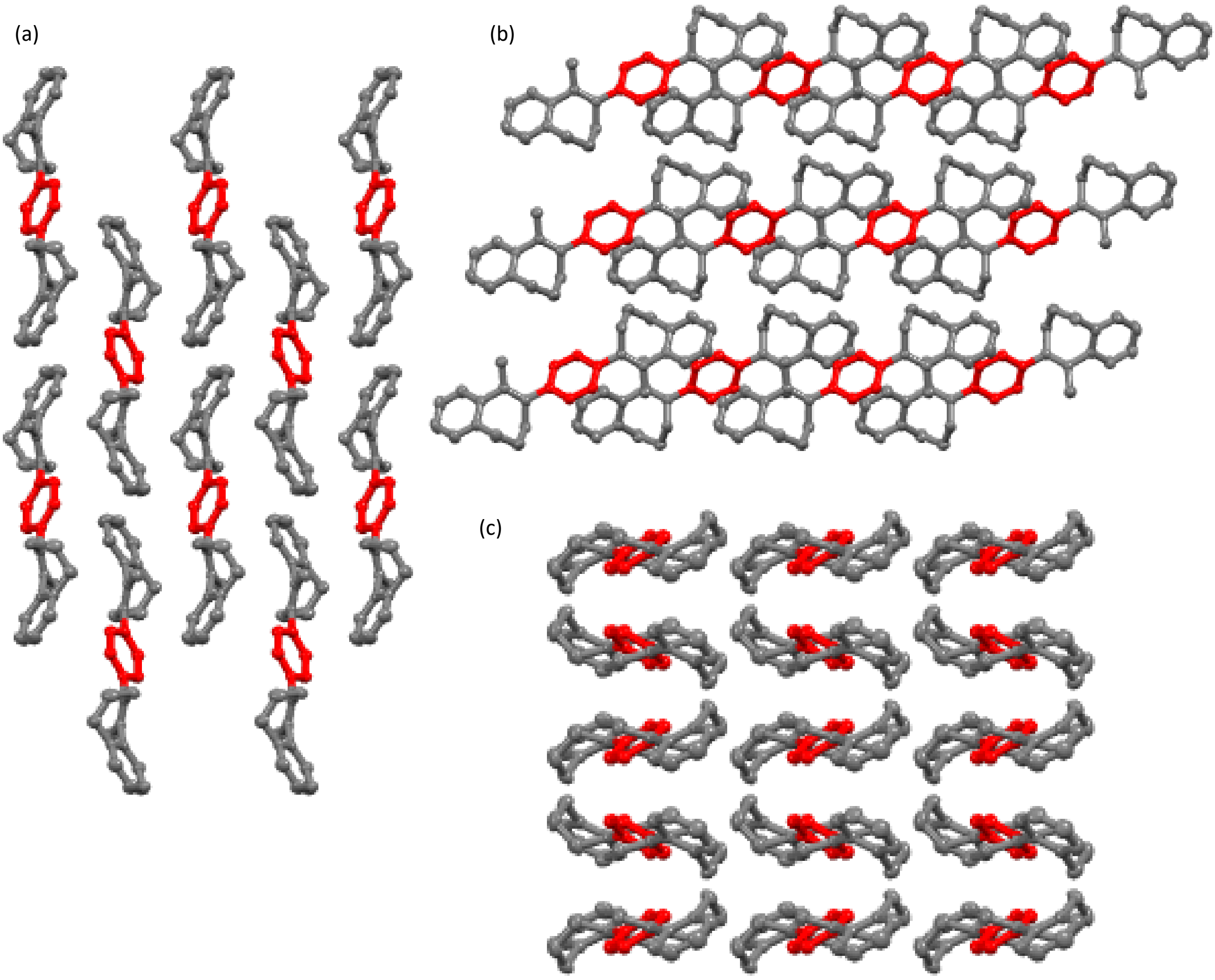


Figure S28. Projection of the structure of **DBαMDB[7]-parallel** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

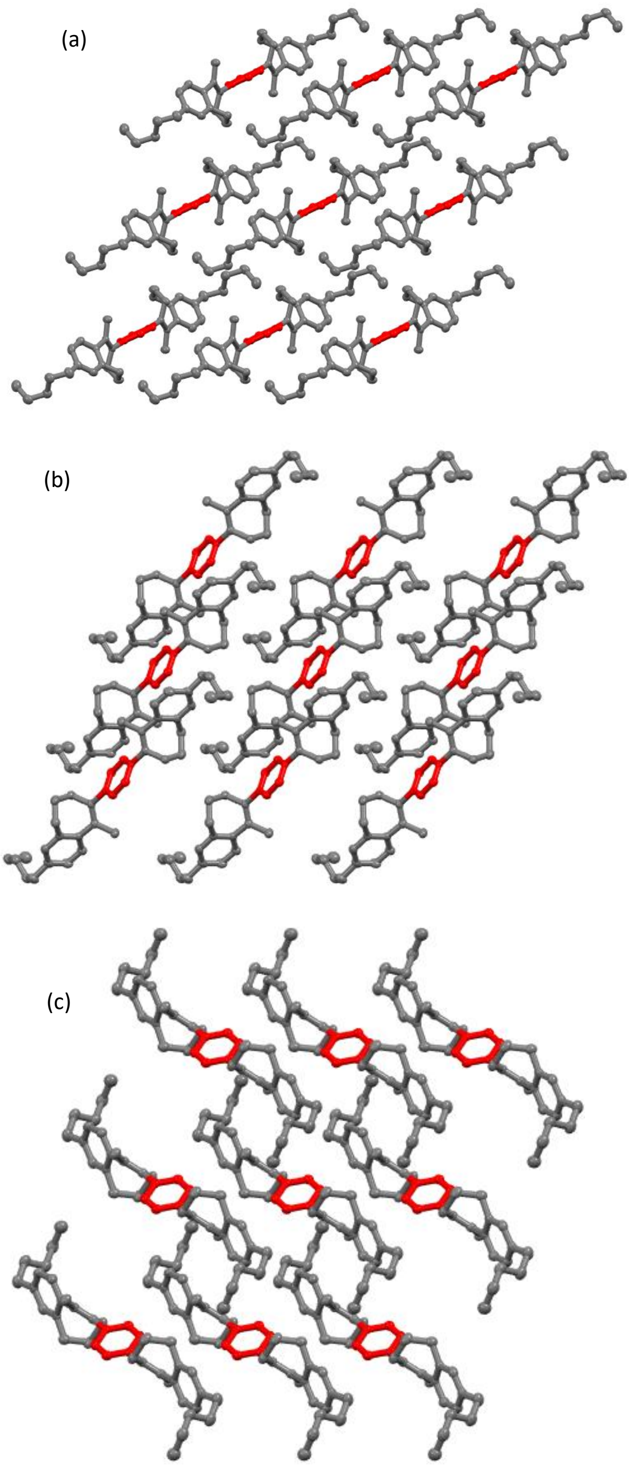


Figure S29. Projection of the structure of **5DBαMDB[7]** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

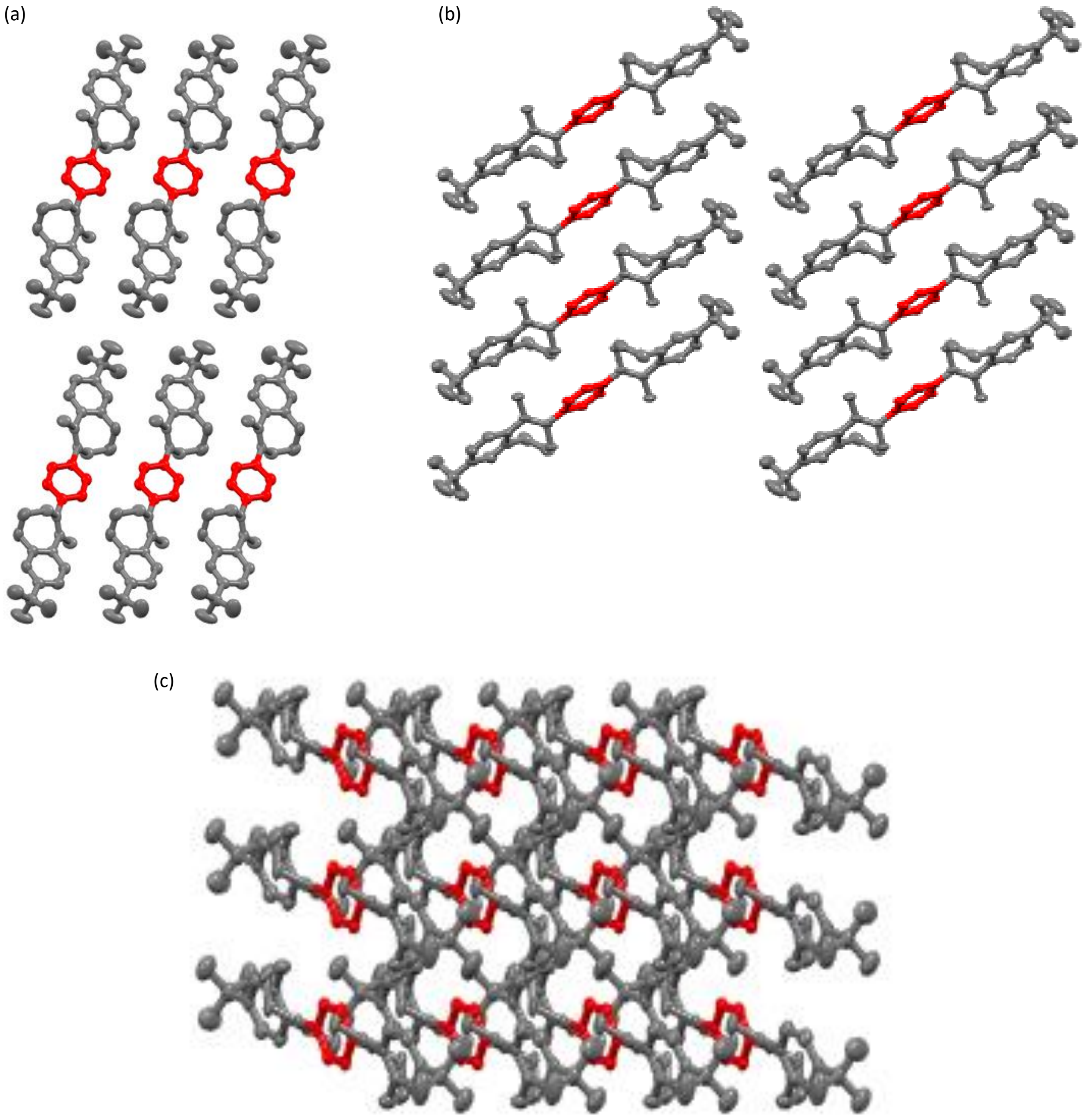


Figure S30. Projection of the structure of **^{t}BuDBαMDB[7]** viewed along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis directions. Hydrogen atoms are omitted for clarity, and the central benzene rings are shown in red.

7. Theoritical study

Molecular and crystal structures used in the computational calculations were from single-crystal X-ray analysis. Calculations of excitation transition of single molecule were performed using Gaussian 09 program, and calculations of NBO analysis were using Gaussian 16 program.

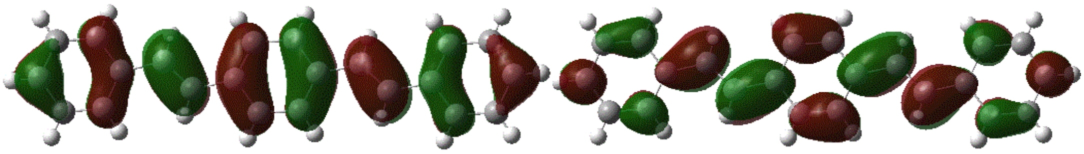
(1) Excitation transition of single molecule

In **5DBαMDB[7]**, methyl groups were used instead of pentyl groups becaouse the calculation did not converge.

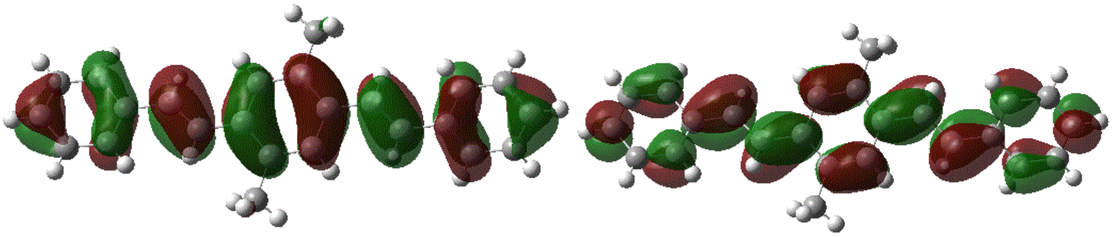
Table S10. Excitation transition properties of each compound.

Entry	Transition property	Oscillator strengths	ΔE [eV]	λ_{abs} [nm]
DSB	0.672 (HOMO→LUMO) 0.184 (HOMO-1→LUMO+1)	1.8823	3.8217	324.42
DSDMB	0.673 (HOMO→LUMO) 0.181 (HOMO-1→LUMO+1)	1.7476	3.6935	335.69
PPB	0.669 (HOMO→LUMO) 0.193 (HOMO-1→LUMO+1)	1.7209	4.2083	294.62
DBDB[6]	0.668 (HOMO→LUMO) 0.205 (HOMO-1→LUMO+1)	1.5320	3.6154	342.93
DBDB[7]	0.664 (HOMO→LUMO) -0.206 (HOMO-1→LUMO+1)	1.4343	4.2444	292.11
DBDMDB[7]	0.477 (HOMO→LUMO) -0.460 (HOMO-1→LUMO+1) -0.125 (HOMO-2→LUMO+2) -0.102 (HOMO-3→LUMO)	1.2504	5.1075	242.75
DBαMDB[7]-cross	0.671 (HOMO→LUMO) 0.238 (HOMO-1→LUMO+1)	1.3063	4.2887	289.10
DBαMDB[7]-parallel	0.652 (HOMO→LUMO) 0.220 (HOMO-1→LUMO+1)	1,2507	4.6772	265.08
5DBαMDB[7]	0.629 (HOMO→LUMO) 0.278 (HOMO-1→LUMO+1)	1.4077	4.6106	268.91
^{t}BuDBαMDB[7]	0.628 (HOMO→LUMO) 0.276 (HOMO-1→LUMO+1) -0.102 (HOMO-3→LUMO+5)	1.5794	4.7347	261.86

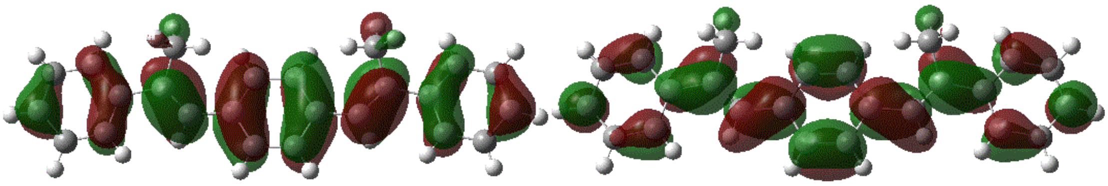
DSB



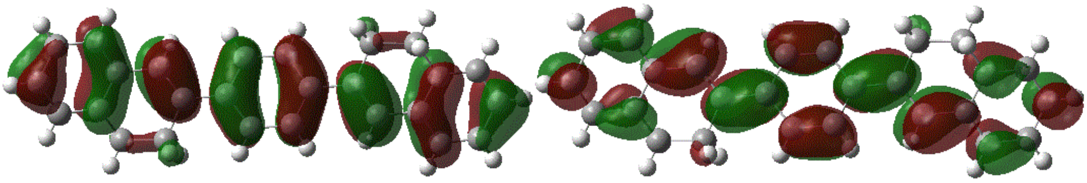
DSDMB



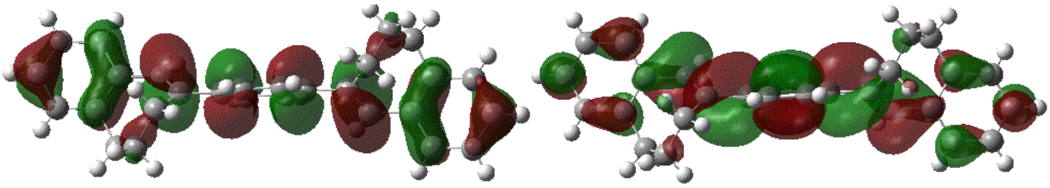
PPB



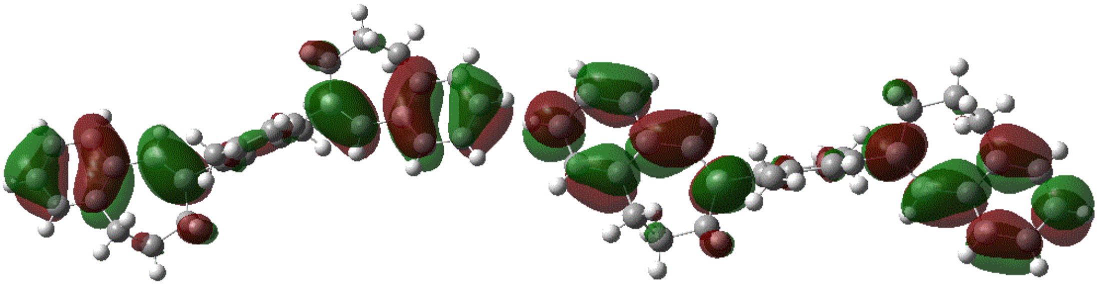
DBDB[6]



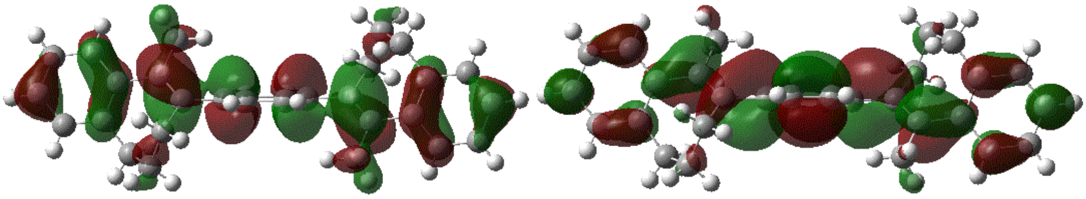
DBDB[7]



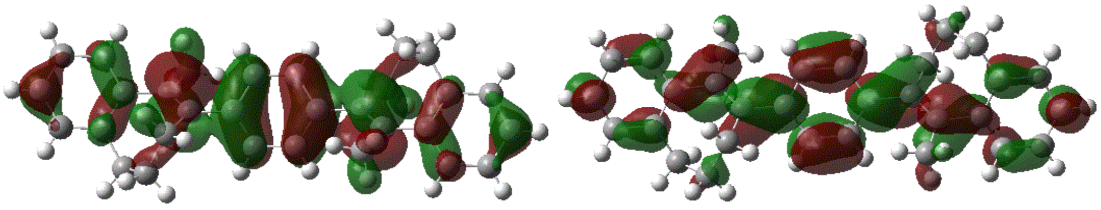
DBDMDB[7]



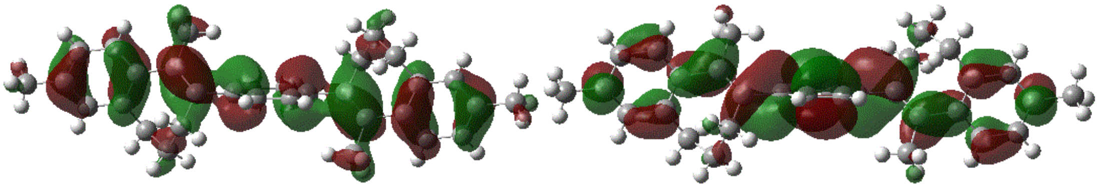
DBαMDB[7]-cross



DBαMDB[7]-parallel



5DBαMDB[7]



***t*BuDBαMDB[7]**

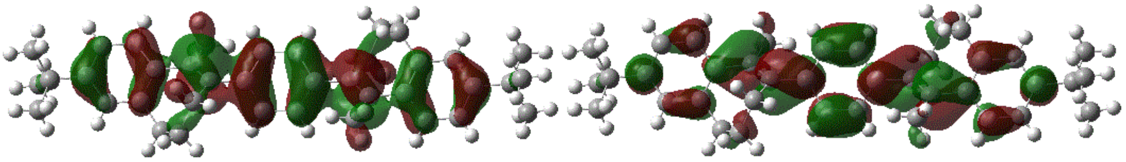


Figure S31. HOMO (left) and LUMO (right) of each compound at single crystal structure.

Table S11. Energy levels of HOMO and LUMO of each compound.

Compound	HOMO [eV]	LUMO [eV]
DSB	-7.18435	-0.15238
DSDMB	-7.07170	-0.16191
PPB	-7.33565	0.24245
DBDB[6]	-6.94897	-0.09497
DBDB[7]	-7.11959	0.53035
DBDMDB[7]	-7.58110	1.31948
DBαMDB[7]-cross	-7.31551	0.53171
DBαMDB[7]-parallel	-7.31279	1.03920
5DBαMDB[7]	-7.33674	1.03784
^{t}BuDBαMDB[7]	-7.41647	0.95185

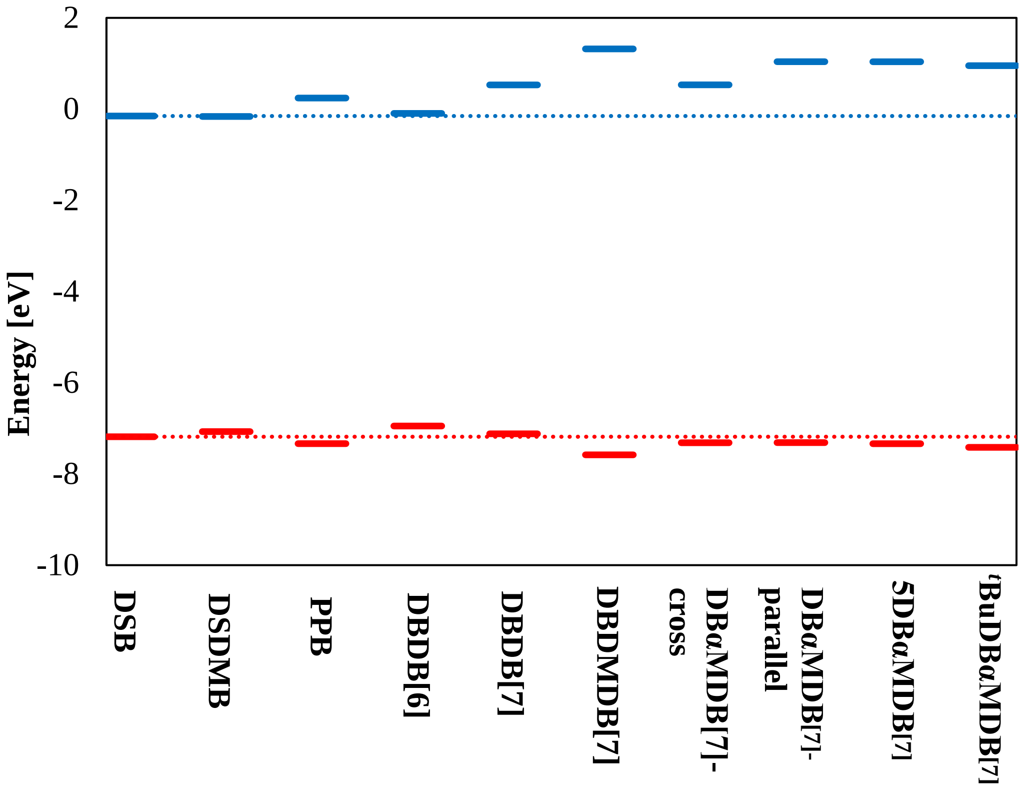
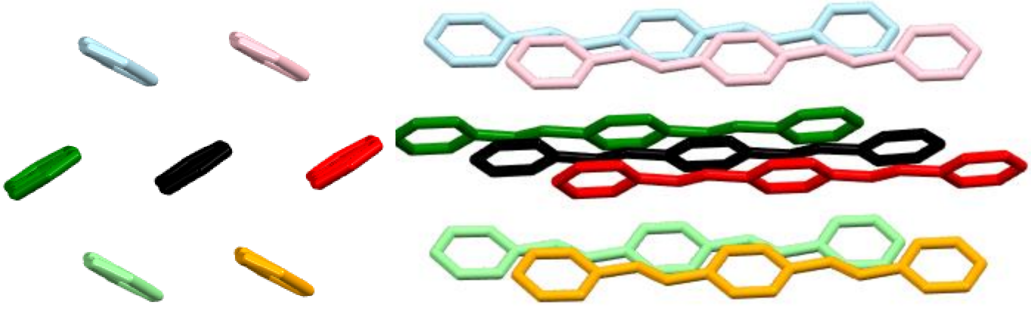


Figure S32. Energy levels of HOMO (red) and LUMO (blue) of each compound.

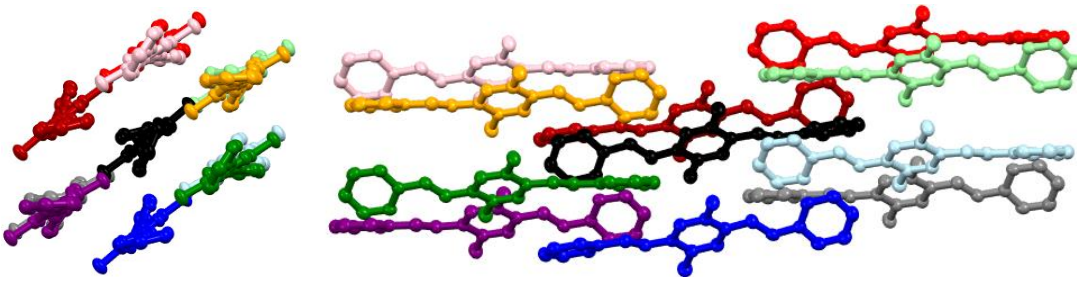
(2) NBO analysis

The center molecule is shown in black. "Unit color A to color B" means the interaction between occupied orbital of C=C bond of color A and unoccupied orbital of C=C bond of color B.



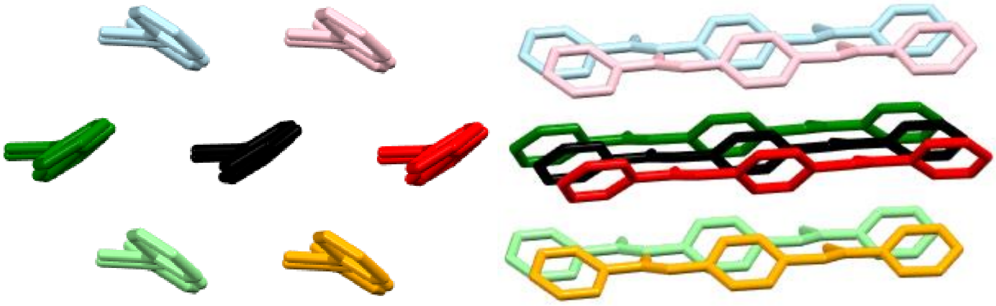
X	Energy [kcal/mol]	
	Unit X to black	Unit black to X
Pink	0.43	0
Red	0.08	0.15
Orange	0.05	0.49
Light green	0.39	0
Green	0.14	0.08
Sky blue	0	0.42

Figure S33. Intermolecular interaction of NBO of **DSB**.



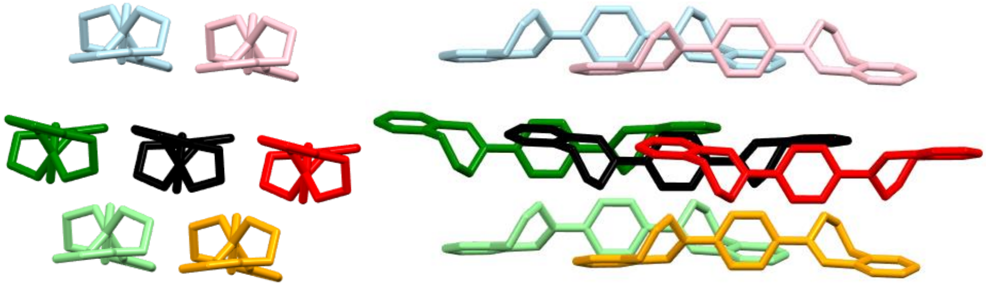
X	Energy [kcal/mol]	
	Unit X to black	Unit black to X
Pink	0.30	0
Red	0.20	0.47
Orange	0	0
Light green	0	0
Green	0	0.30
Sky blue	0.47	0.19
Blue	0.36	0.36
Purple	0	0
Gray	0	0
Brown	0.63	0.61

Figure S34. Intermolecular interaction of NBO of **DSDMB**.



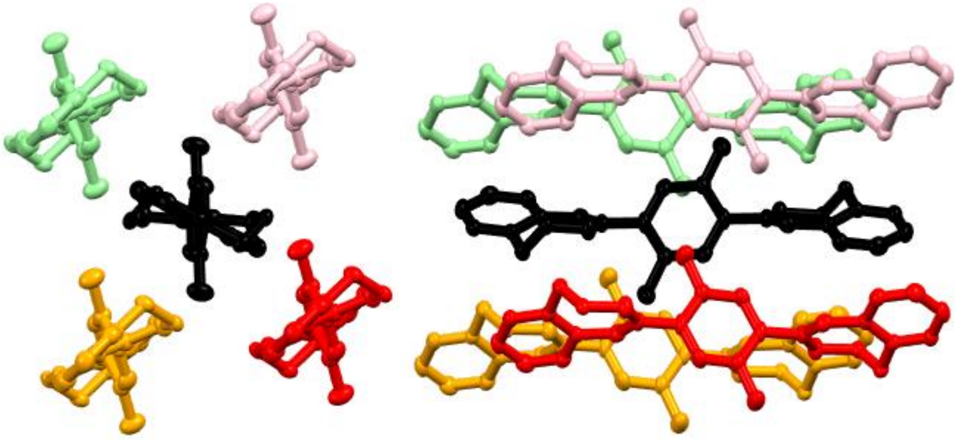
X	Energy [kcal/mol]	
	Unit X to black	Unit black to X
Pink	0.14	0
Red	0	0
Orange	0	0.31
Light green	0.20	0.11
Green	0	0
Sky blue	0	0.15

Figure S35. Intermolecular interaction of NBO of **PPB**.



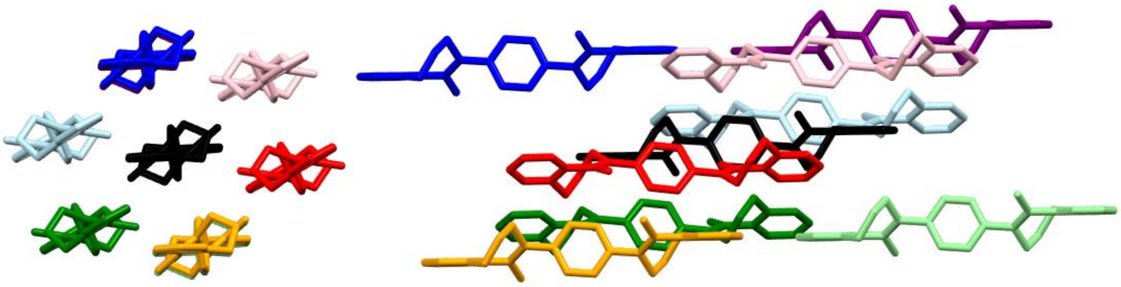
X	Energy [kcal/mol]	
	Unit X to black	Unit black to X
Pink	0.41	0.41
Red	0	0
Orange	0.42	0.42
Light green	0.52	0.52
Green	0	0
Sky blue	0.16	0.16

Figure S36. Intermolecular interaction of NBO of **DBDB[7]**.



X	Energy [kcal/mol]	
	Unit X to black	Unit black to X
Pink	0	0
Red	0	0
Orange	0	0
Light green	0	0

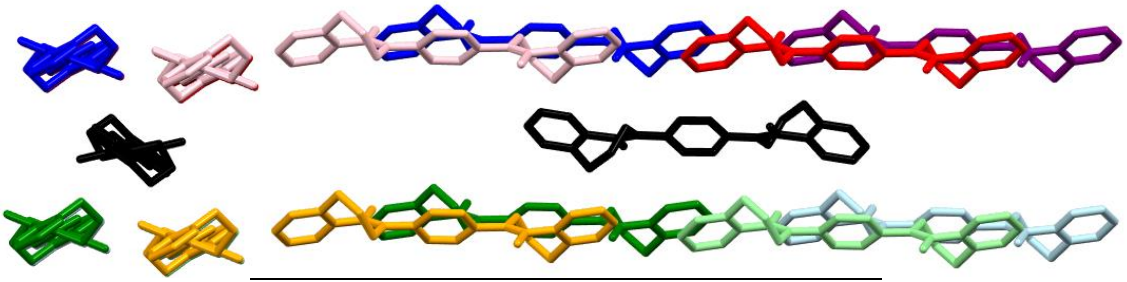
Figure S37. Intermolecular interaction of NBO of **DBDMDB[7]**.



X	Energy [kcal/mol]	
	Unit X to black	Unit black to X
Pink	0.28	0.15
Red	0.15	0.19
Orange	0	0
Light green	0	0
Green	0.19	0.15
Sky blue	0.15	0.28

Blue	0	0
Purple	0	0

Figure S38. Intermolecular interaction of NBO of **DBαMDB[7]-cross**.



X	Energy [kcal/mol]	
	Unit X to black	Unit black to X
Pink	0	0
Red	0	0.08
Orange	0	0
Light green	0.07	0
Green	0	0.14
Sky blue	0	0
Blue	0.13	0
Purple	0	0

Figure S39. Intermolecular interaction of NBO of **DBαMDB[7]-parallel**.

8. References

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12. S. Varghese, S. K. Park, S. Casado, R. C. Fischer, R. Resel, B. M-Medina, R. Wannemacher, S. Y. Park, and J. Gierschner, *J. Phys. Chem. Lett*, 2013, **4**, 10, 1597-1602. DOI: 10.1021/jz400659b

9. NMR chart

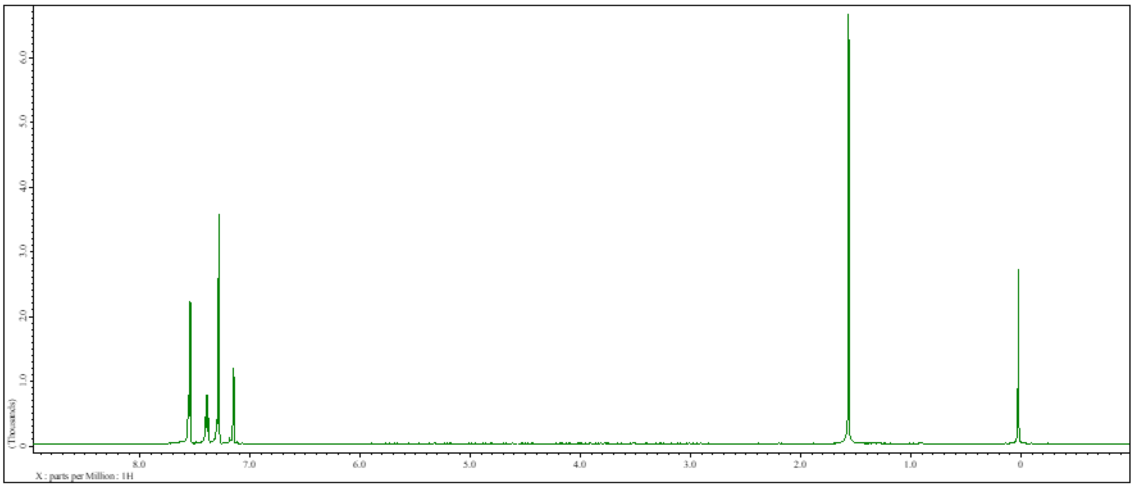

Figure S40. ^{1}H-NMR spectra of **DSB** (500 MHz, $CDCl_3$).

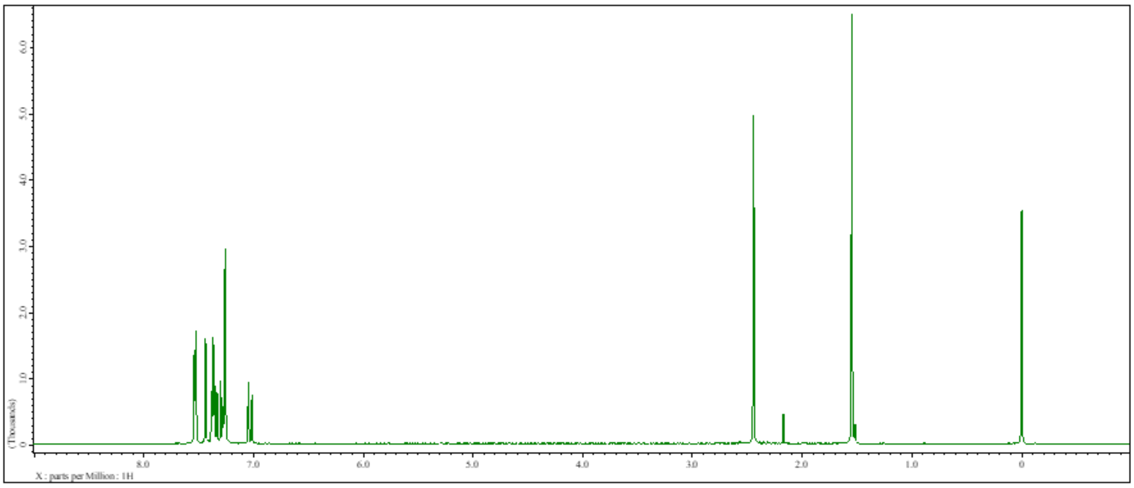

Figure S41. ^{1}H-NMR spectra of **DSDMB** (500 MHz, $CDCl_3$).

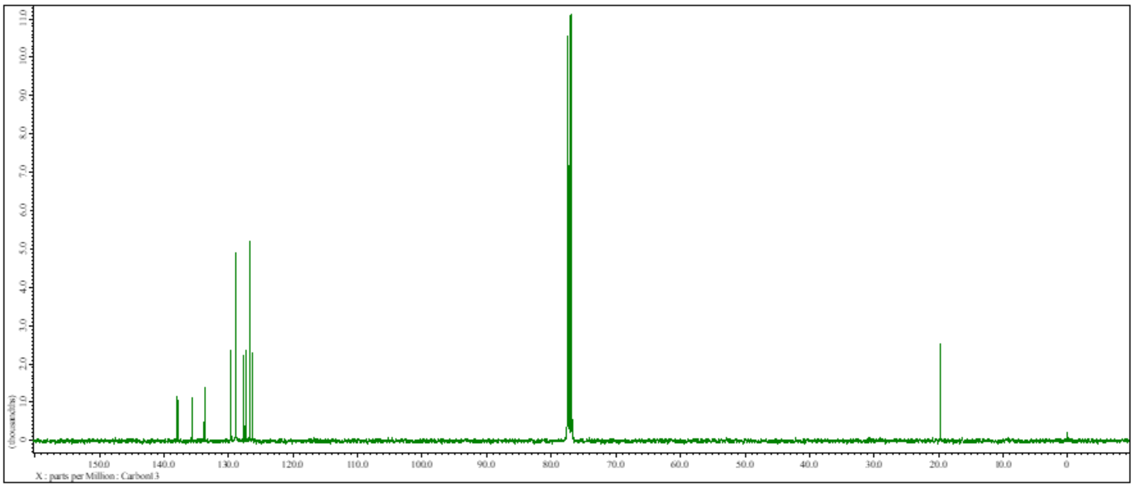

Figure S42. ^{13}C-NMR spectra of **DSDMB** (100 MHz, $CDCl_3$).

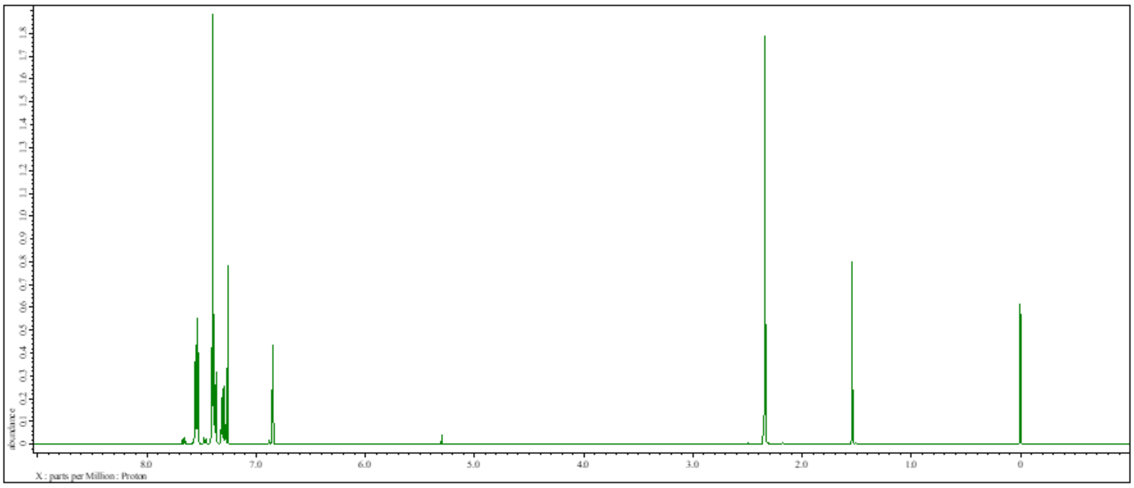

Figure S43. ^{1}H-NMR spectra of **PPB** (399 MHz, $CDCl_3$).

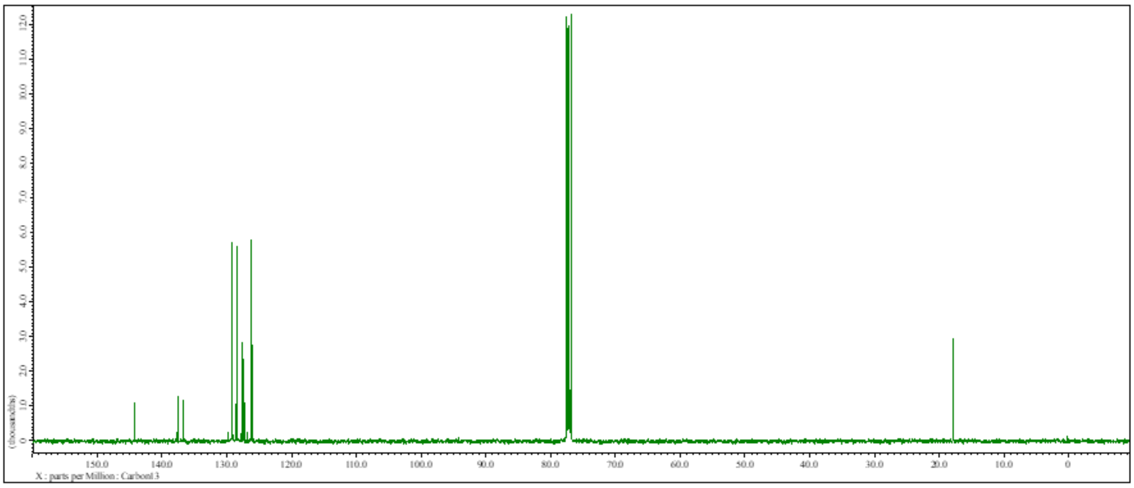

Figure S44. ^{13}C-NMR spectra of **PPB** (100 MHz, $CDCl_3$).

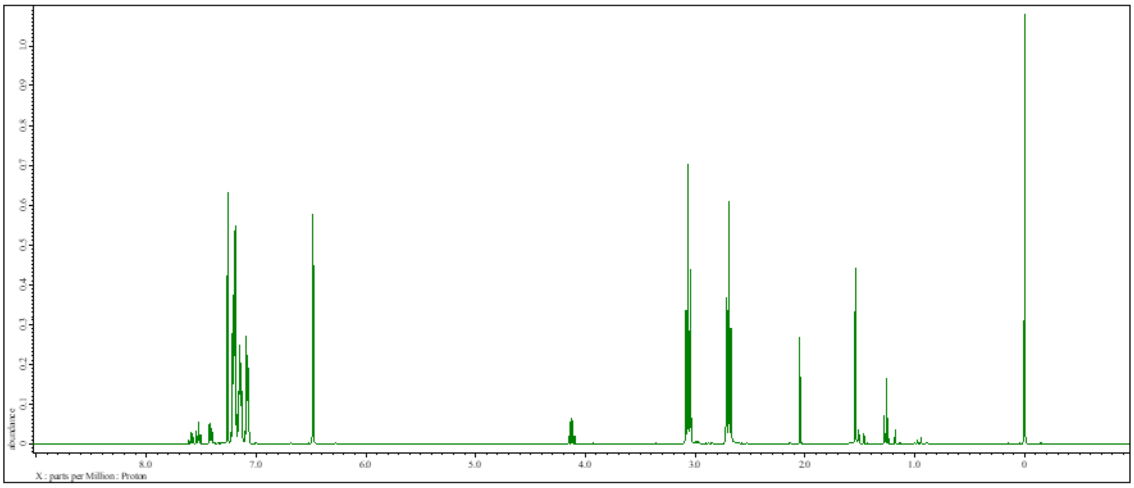

Figure S45. ^{1}H-NMR spectra of **4** (399 MHz, $CDCl_3$).

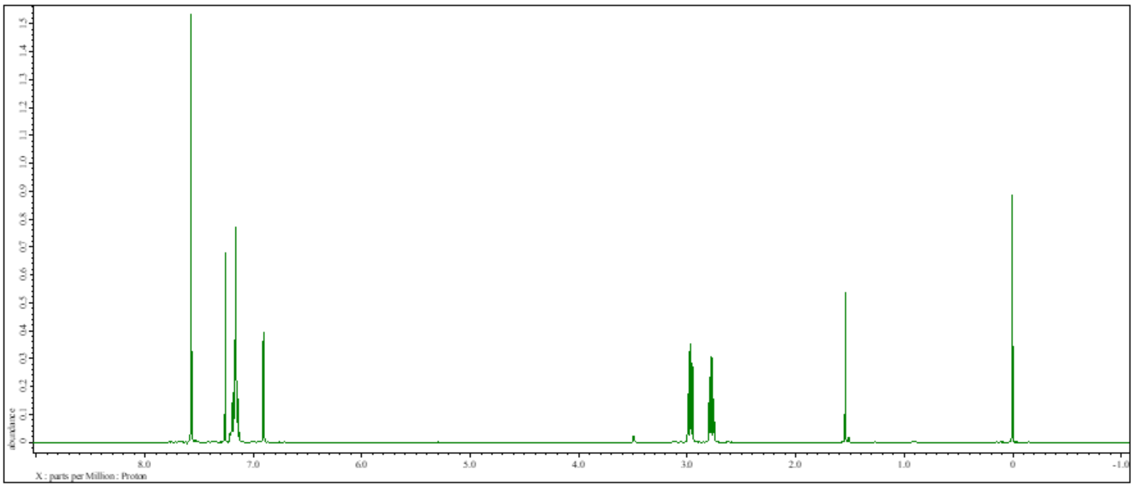

Figure S46. ^{1}H-NMR spectra of **DBDB[6]** (399 MHz, CDCl$_3$).

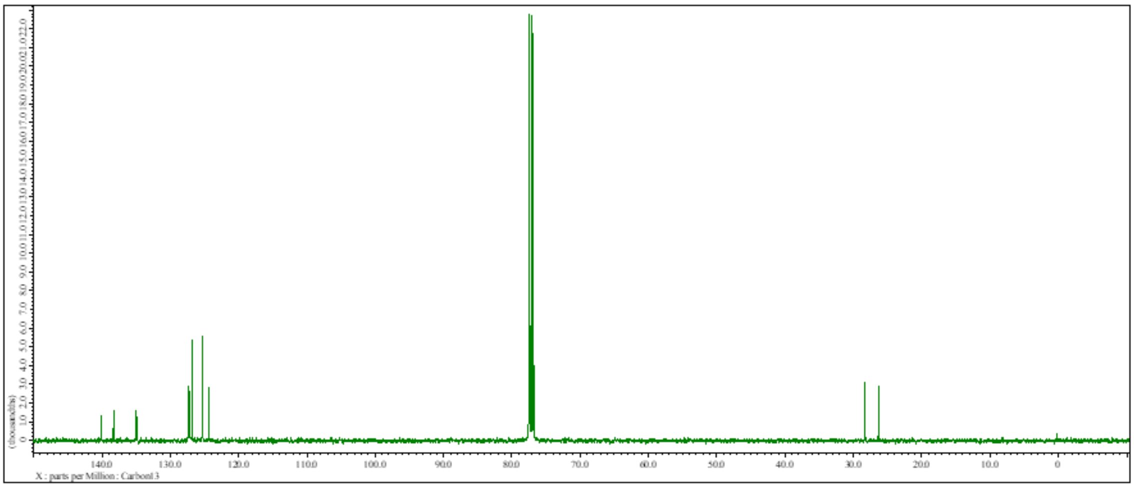

Figure S47. ^{13}C-NMR spectra of **DBDB[6]** (100 MHz, CDCl$_3$).

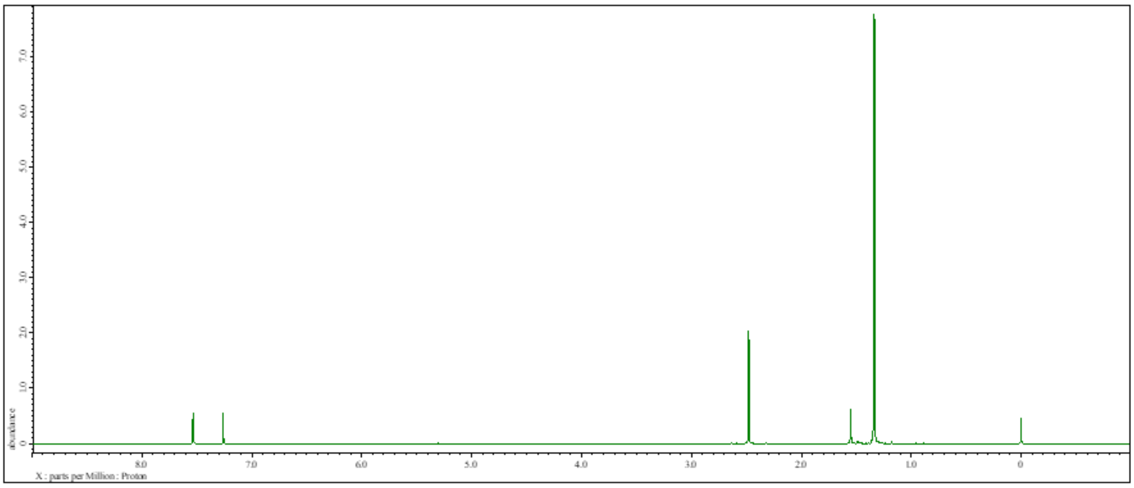

Figure S48. ^{1}H-NMR spectra of **DMB-B(pin)** (399 MHz, CDCl$_3$),

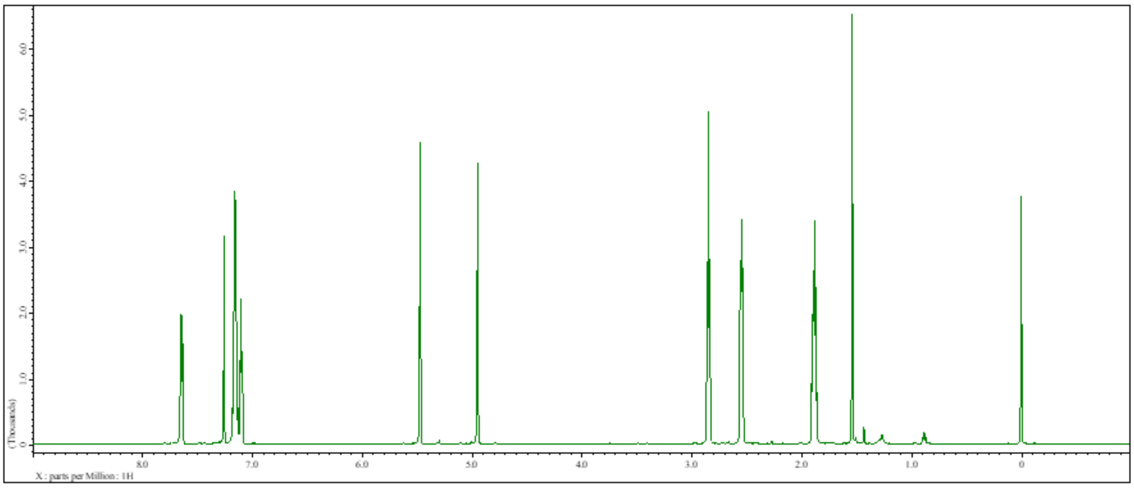

Figure S49. ^{1}H-NMR spectra of **7a** (500 MHz, $CDCl_3$).

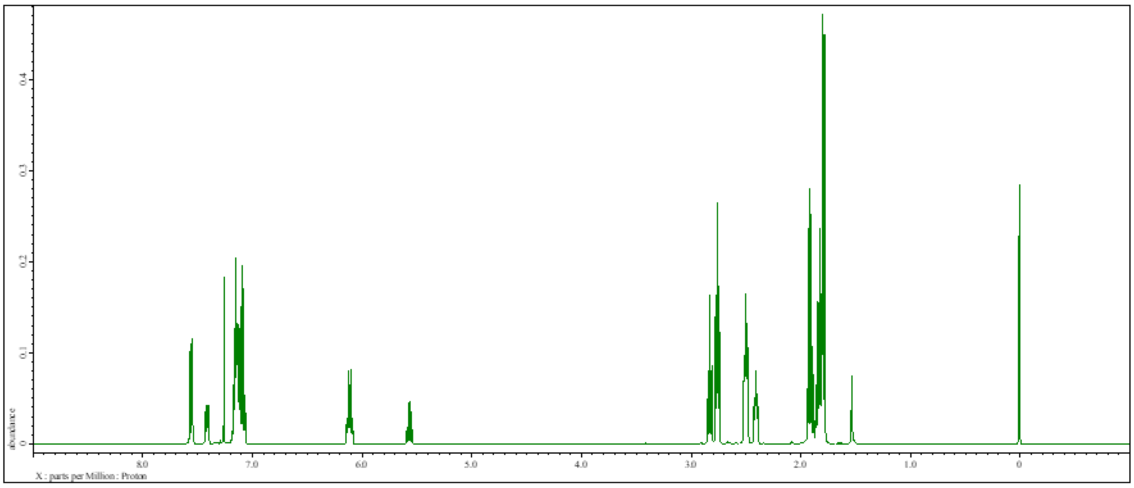

Figure S50. ^{1}H-NMR spectra of **7b** (399 MHz, $CDCl_3$).

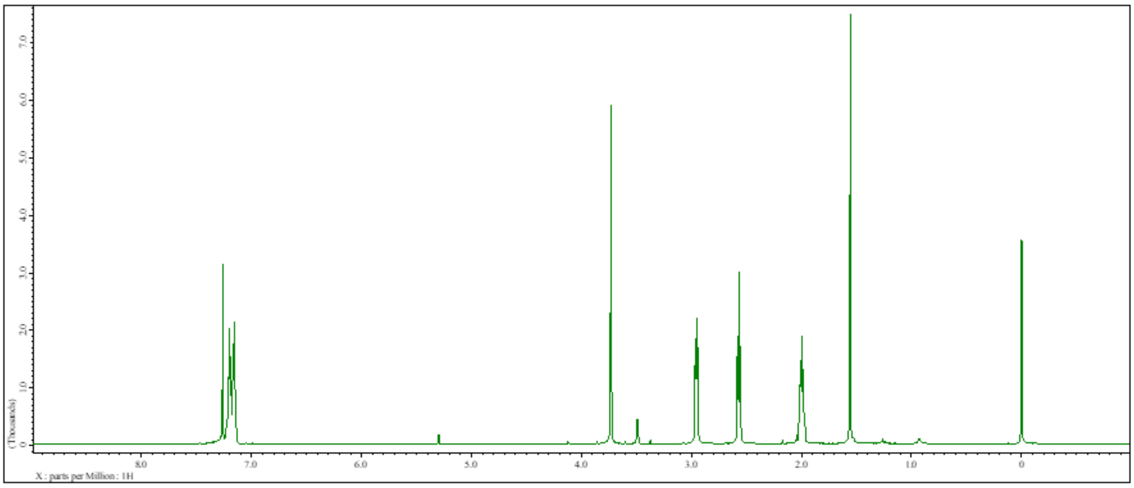

Figure S51. ^{1}H-NMR spectra of **8a** (500 MHz, $CDCl_3$).

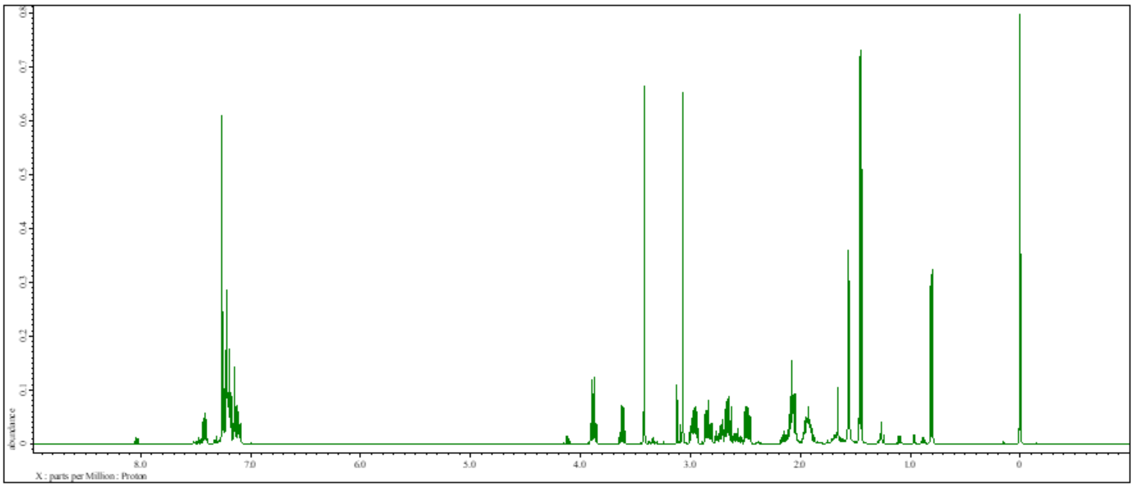

Figure S52. ^{1}H-NMR spectra of **8b** (399 MHz, $CDCl_3$).

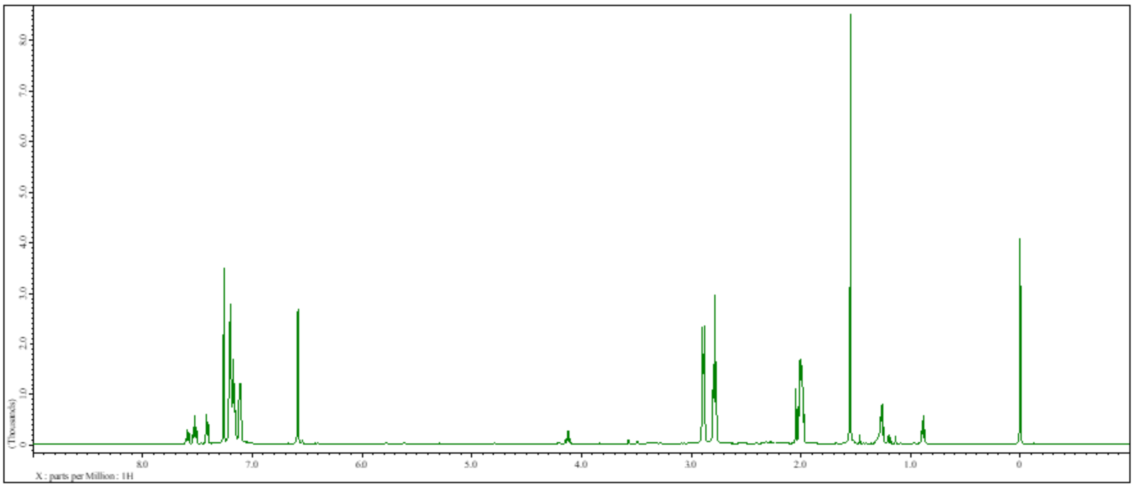

Figure S53. ^{1}H-NMR spectra of **9a** (500 MHz, $CDCl_3$).

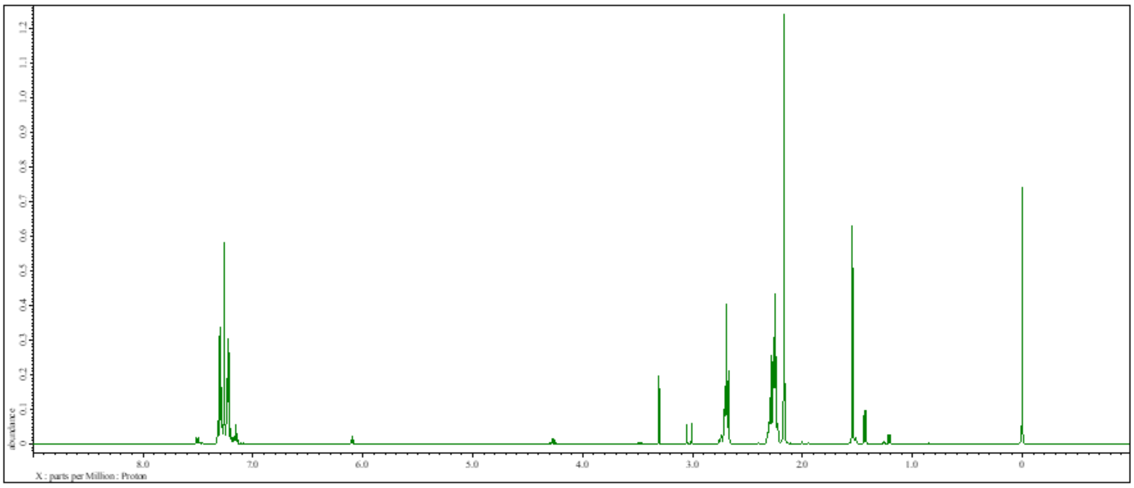

Figure S54. ^{1}H-NMR spectra of **9b** (399 MHz, $CDCl_3$).

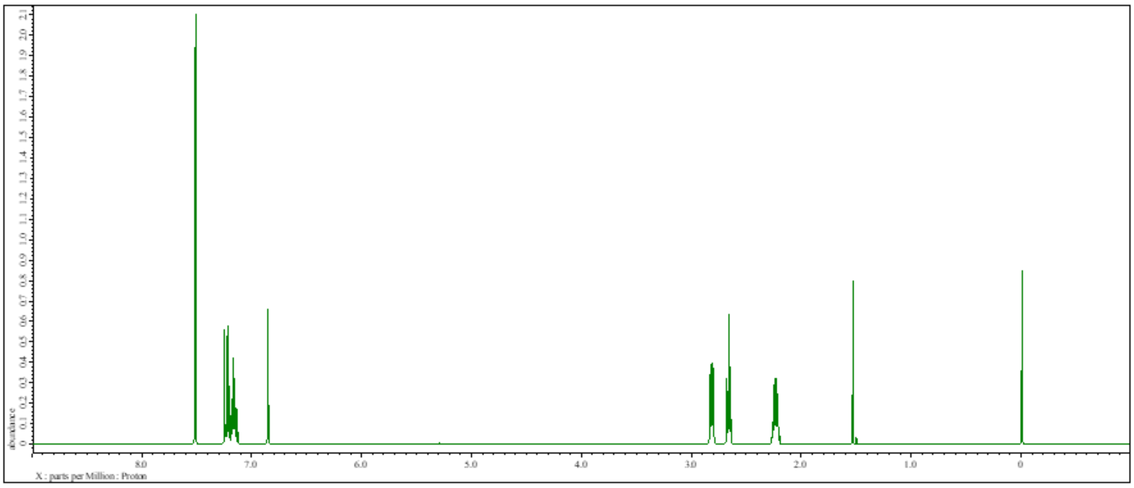

Figure S55. ^{1}H-NMR spectra of **DBDB[7]** (399 MHz, CDCl$_3$).

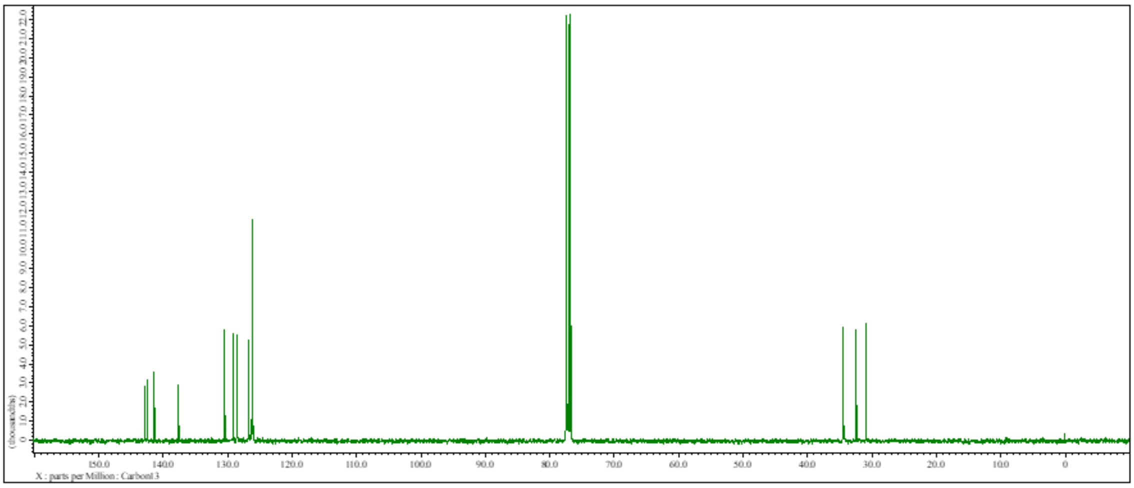

Figure S56. ^{13}C-NMR spectra of **DBDB[7]** (100 MHz, CDCl$_3$)

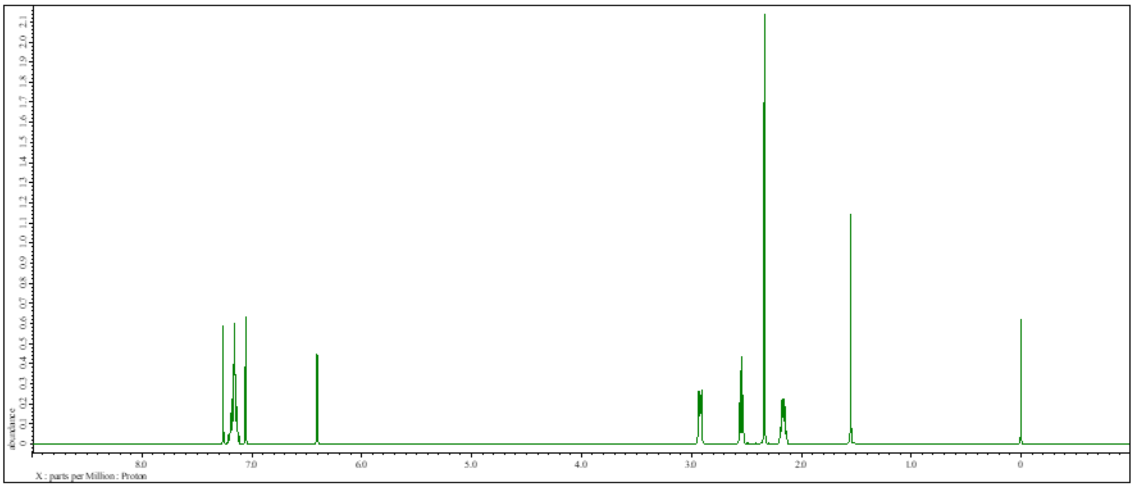

Figure S57. ^{1}H-NMR spectra of **DBDMDB[7]** (399 MHz, CDCl$_3$).

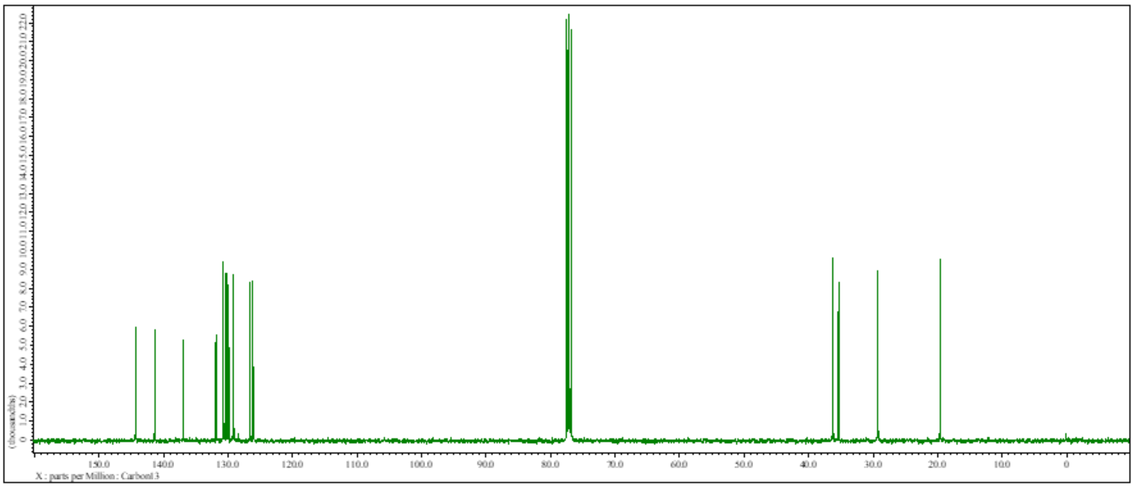

Figure S58. ^{13}C-NMR spectra of **DBDMDB[7]** (100 MHz, CDCl$_3$).

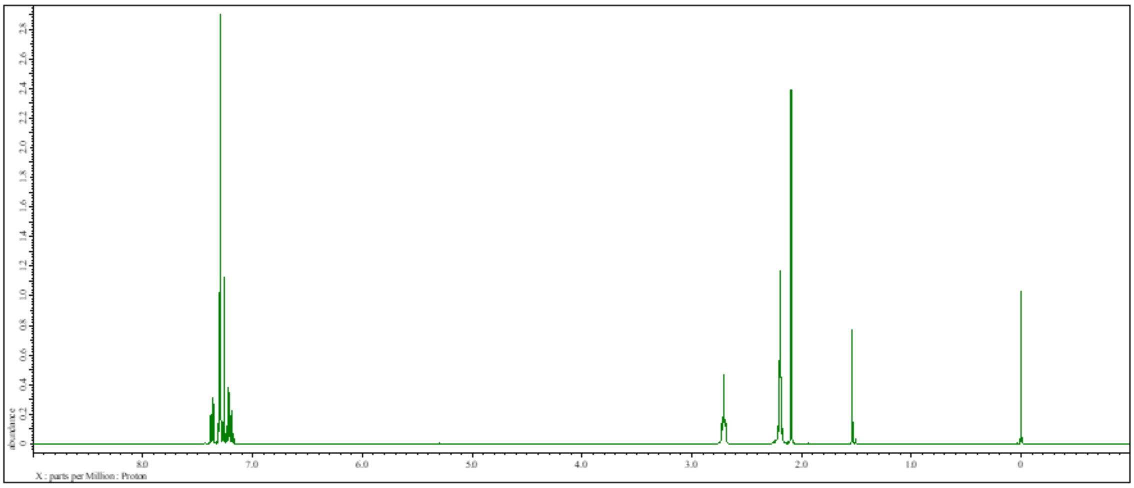

Figure S59. ^{1}H-NMR spectra of **DBαMDB[7]** (399 MHz, CDCl$_3$).

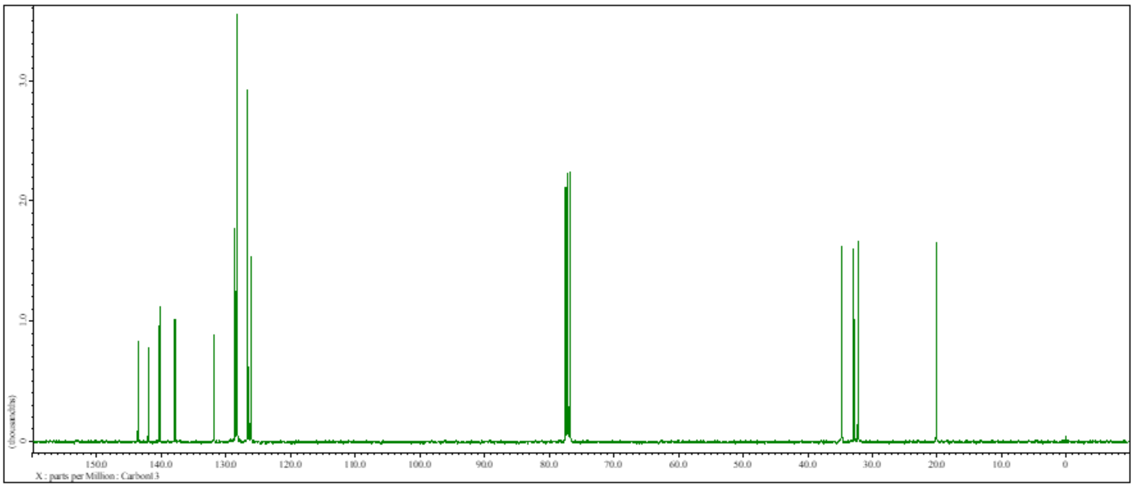

Figure S60. ^{1}H-NMR spectra of **DBαMDB[7]** (100MHz, CDCl$_3$).

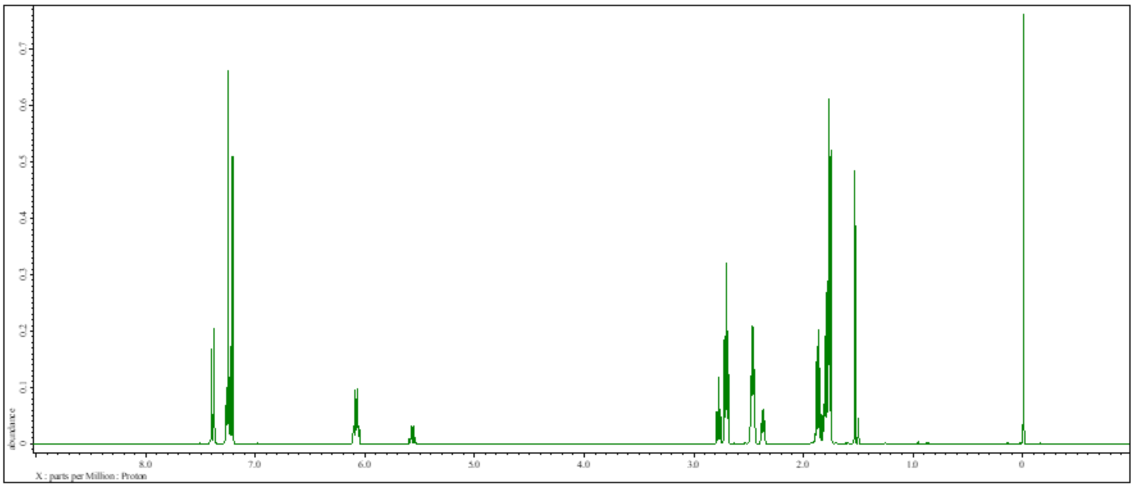

Figure S61. ^{1}H-NMR spectra of **11** (399 MHz, $CDCl_3$).

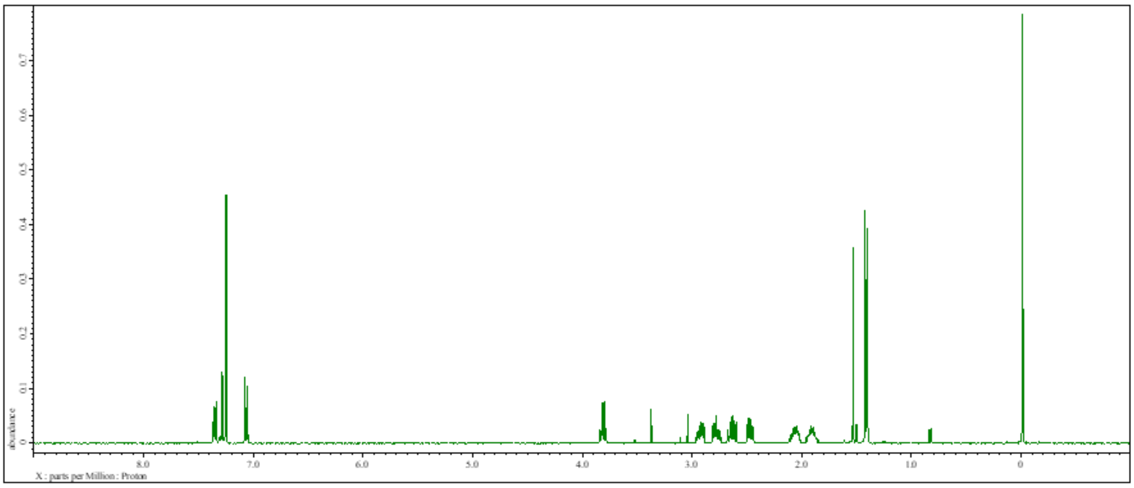

Figure S62. ^{1}H-NMR spectra of **12** (399 MHz, $CDCl_3$).

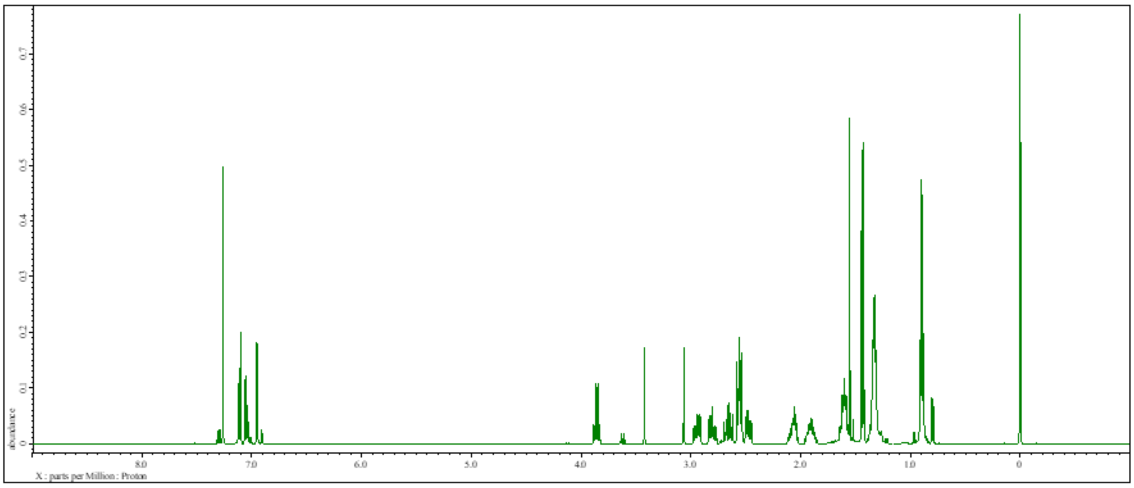

Figure S63. ^{1}H-NMR spectra of **13** (399 MHz, $CDCl_3$).

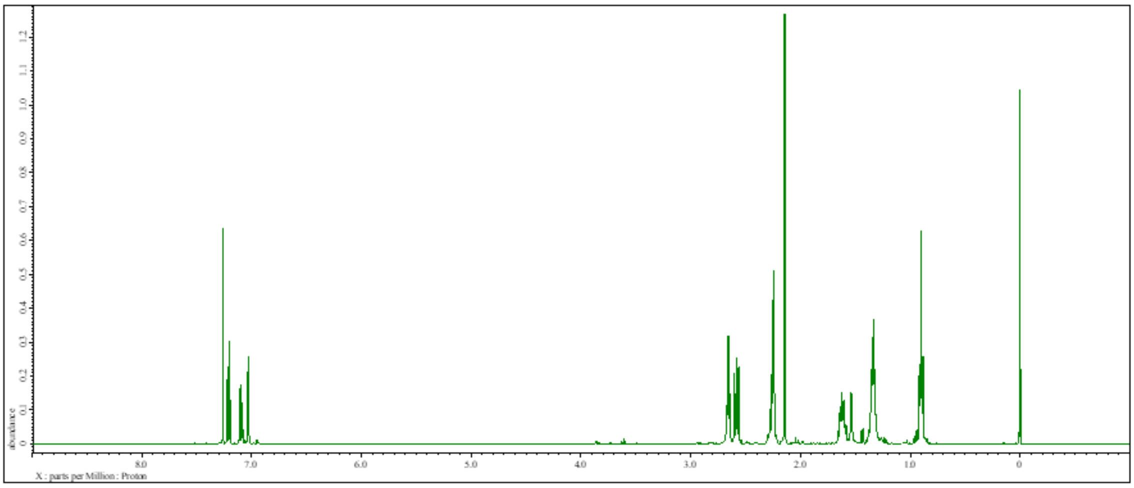

Figure S64. ^{1}H-NMR spectra of **14** (399 MHz, $CDCl_3$).

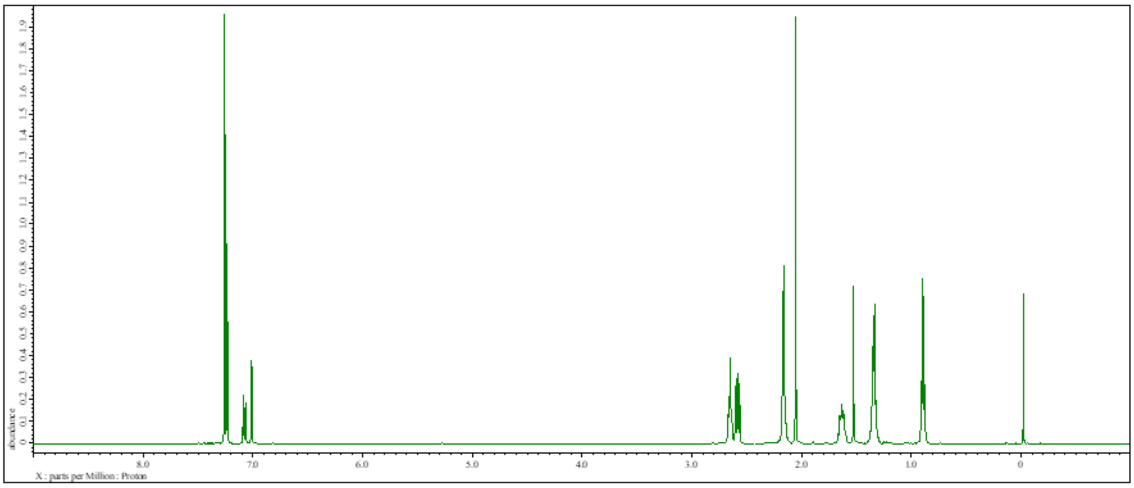

Figure S65. ^{1}H-NMR spectra of **5DBαMDB[7]** (399 MHz, $CDCl_3$).

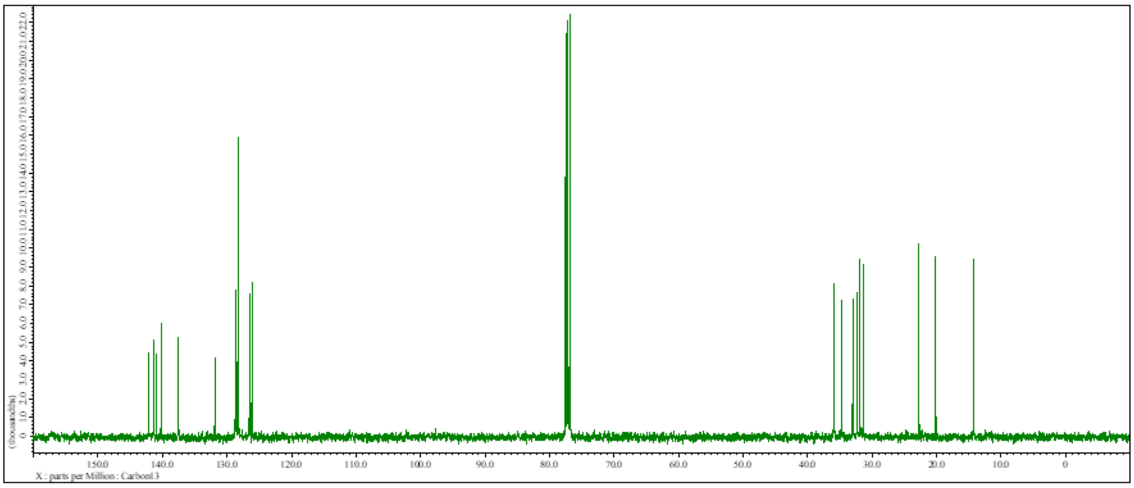

Figure S66. ^{13}C-NMR spectra of **5DBαMDB[7]** (100 MHz, $CDCl_3$).

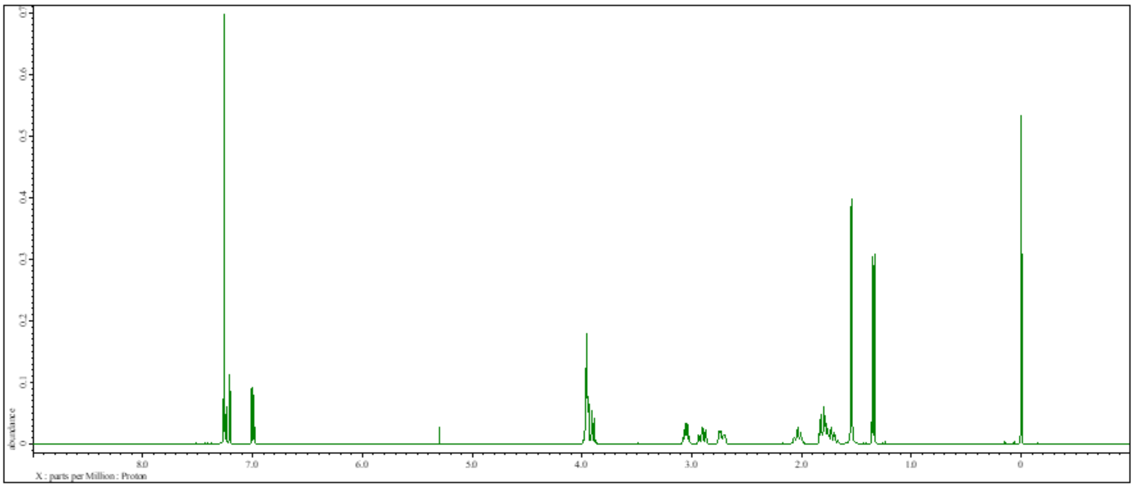

Figure S67. ^{1}H-NMR spectra of **15** (399 MHz, $CDCl_3$).

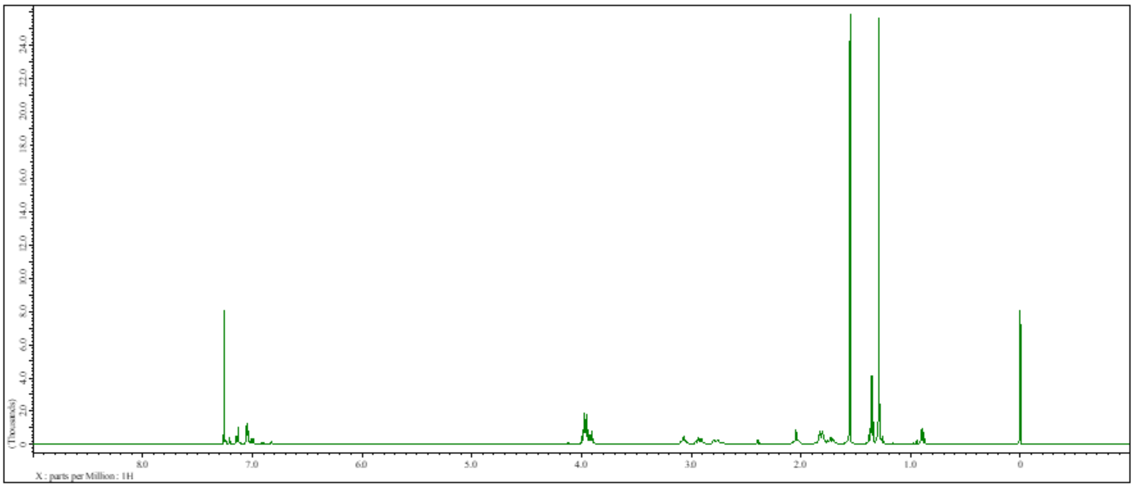

Figure S68. ^{1}H-NMR spectra of **16** (500 MHz, $CDCl_3$).

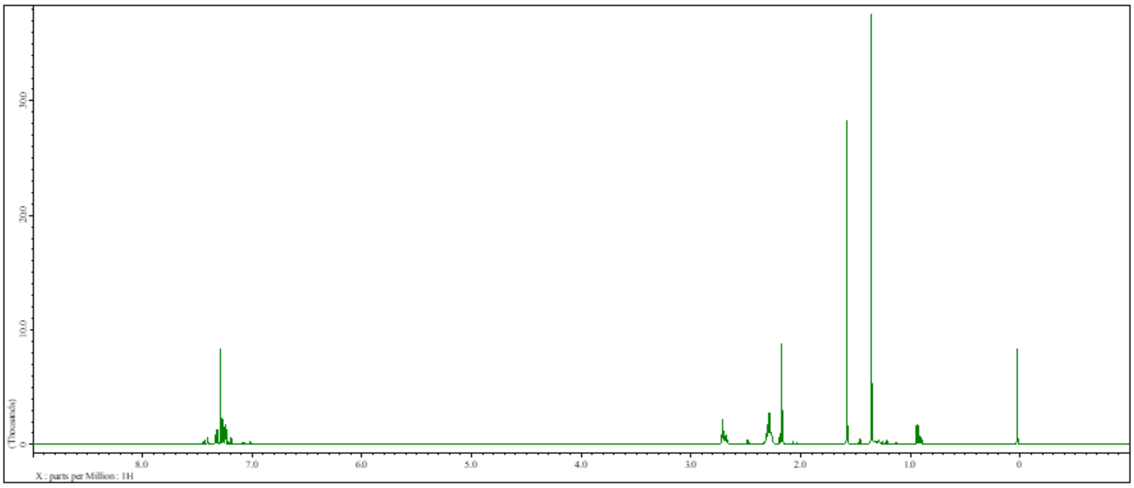

Figure S69. ^{1}H-NMR spectra of **18** (500 MHz, $CDCl_3$).

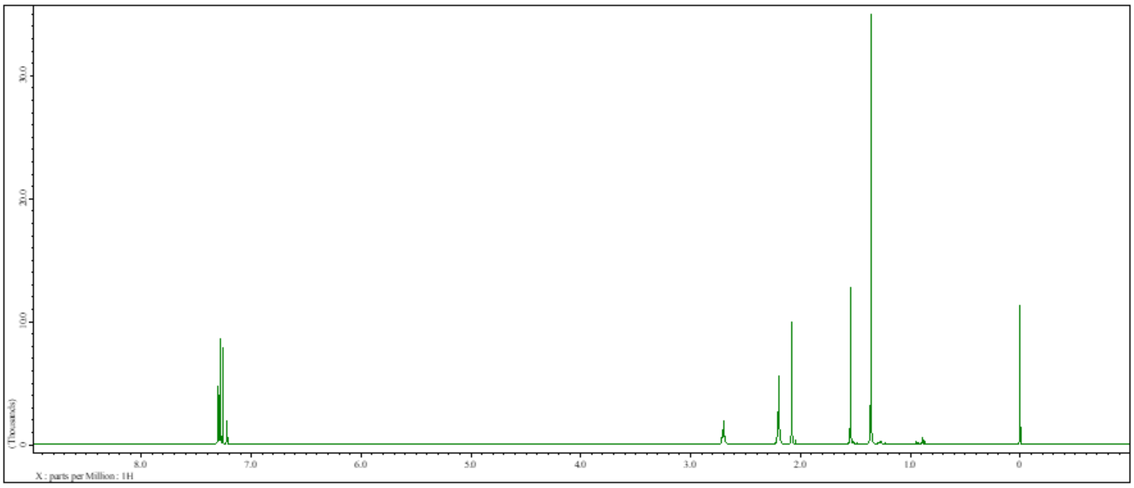

Figure S70. ^{1}H-NMR spectra of **^{t}BuDBαMDB[7]** (500 MHz, $CDCl_3$).

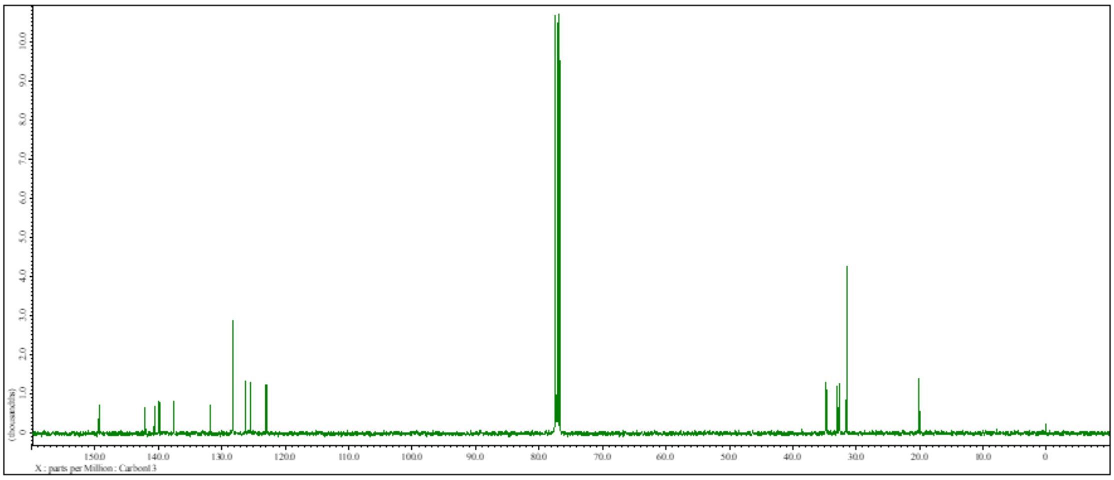

Figure S71. ^{13}C-NMR spectra of **^{t}BuDBαMDB[7]** (100 MHz, $CDCl_3$).

10. High resolution mass spectrometry (HRMS) chart

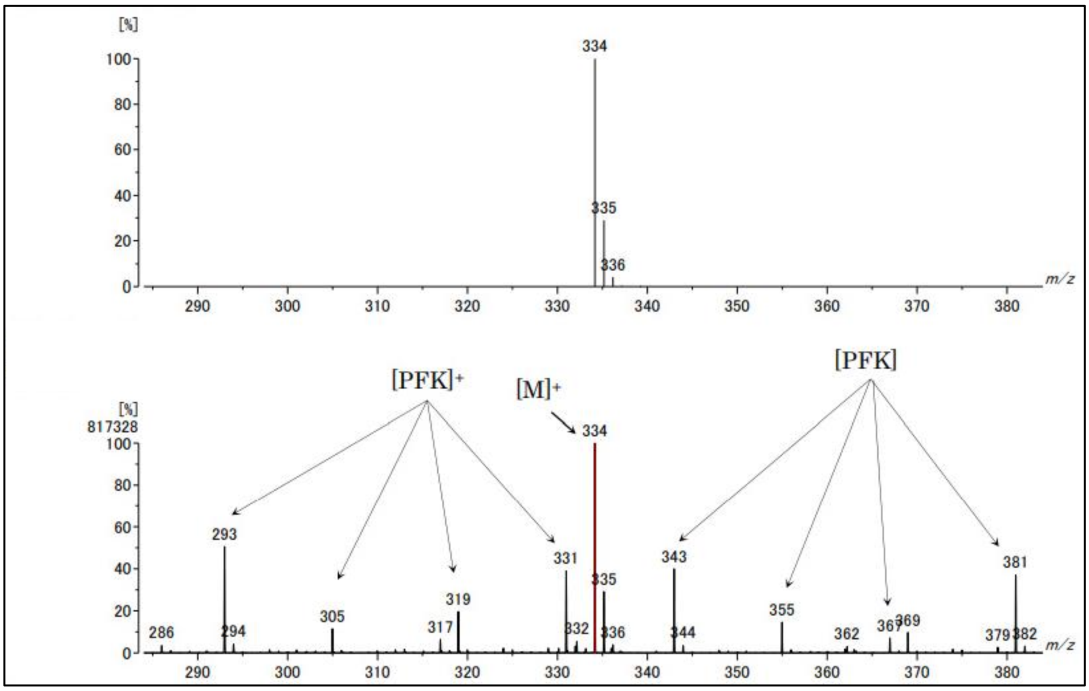

Figure S72. HR-MS spectra of **DBDB[6]** (above: calculated data; below: experimental data).

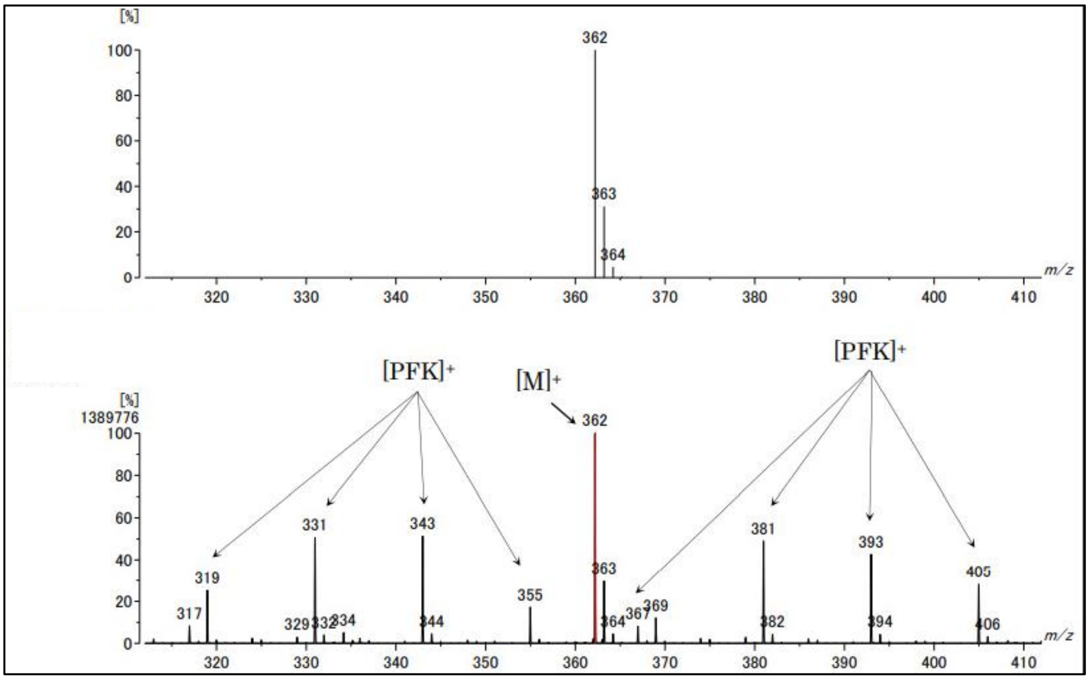

Figure S73. HR-MS spectra of **DBDB[7]** (above: calculated data; below: experimental data).

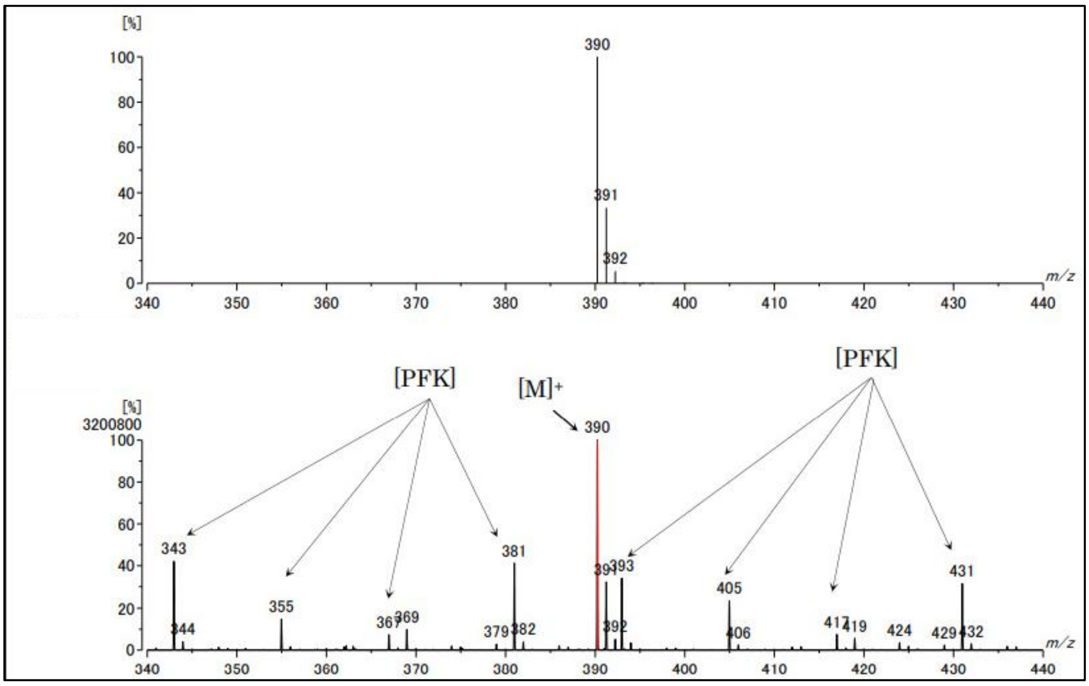

Figure S74. HR-MS spectra of **DBDMDB[7]** (above: calculated data; below: experimental data).

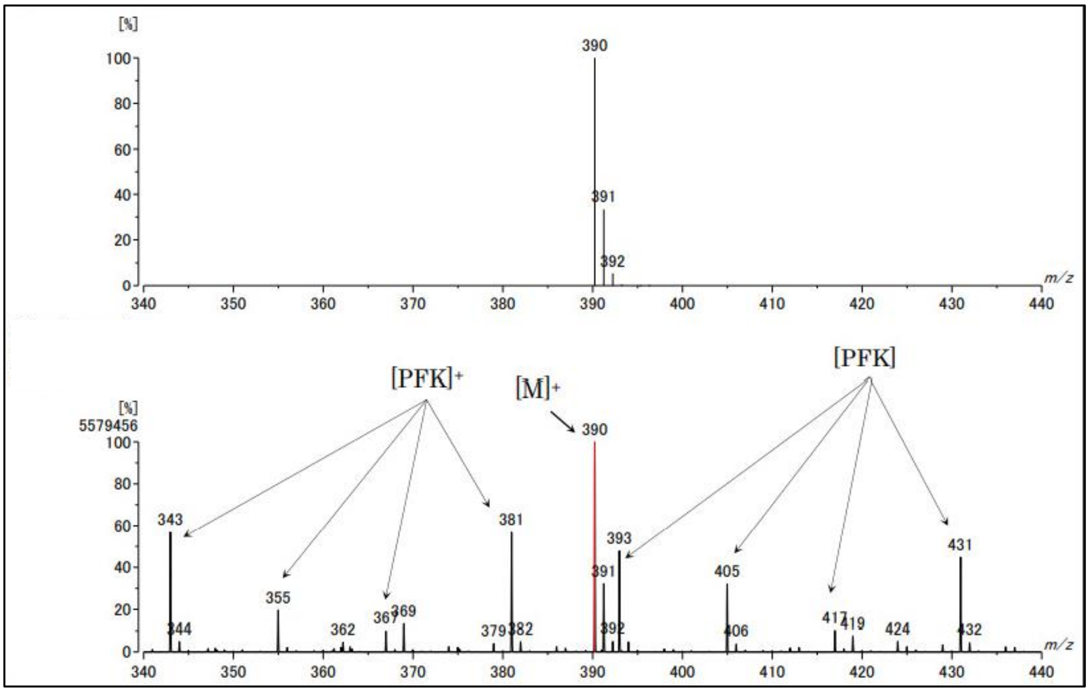

Figure S75. HR-MS spectra of **DBαMDB[7]** (above: calculated data; below: experimental data).

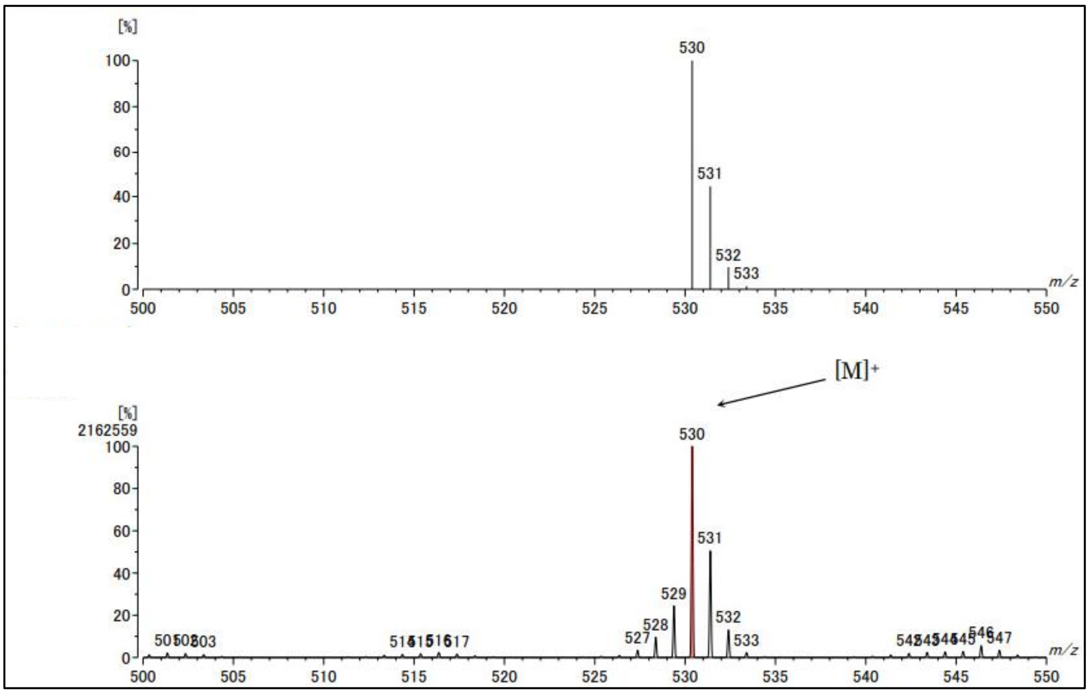

Figure S76. HR-MS spectra of **5DBαMDB[7]** (above: calculated data; below: experimental deta).

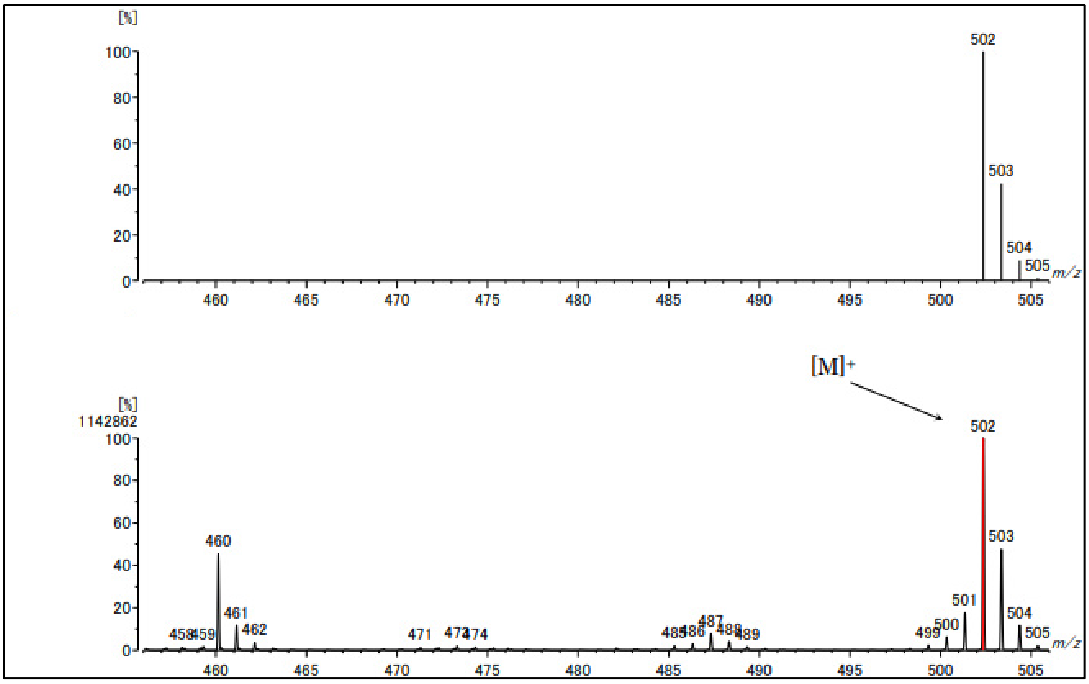

Figure S77. HR-MS spectra of **^{t}BuDBαMDB[7]** (above: calculated data; below: experimental data).

Crystal Structures (Cambridge Crystallographic Data Centre)

CCDC 2168494-2168501

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: DBDB7

```
Bond precision:   C-C = 0.0027 A           Wavelength=0.71073

Cell:            a=7.8987(6)       b=9.0080(6)       c=13.8356(14)
                 alpha=99.206(7)   beta=102.460(8)   gamma=90.999(6)
Temperature:     100 K

                  Calculated                  Reported
Volume            947.48(14)                  947.48(14)
Space group       P -1                        P -1
Hall group        -P 1                        -P 1
Moiety formula    C28 H26                     C28 H26
Sum formula       C28 H26                     C28 H26
Mr                362.49                      362.49
Dx,g cm-3         1.271                       1.271
Z                 2                           2
Mu (mm-1)         0.071                       0.071
F000              388.0                       388.0
F000'             388.14
h,k,lmax          11,13,20                    11,13,19
Nref              6095                        5227
Tmin,Tmax         0.992,0.999                 0.784,1.000
Tmin'             0.979

Correction method= # Reported T Limits: Tmin=0.784 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.858            Theta(max)= 31.103

                                                       wR2(reflections)=
R(reflections)= 0.0758( 3984)                          0.1698( 5227)

S = 1.092                  Npar= 253
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The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

```
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PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          3 Note
PLAT767_ALERT_4_G INS Embedded LIST 6 Instruction Should be LIST 4     Please Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.2 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

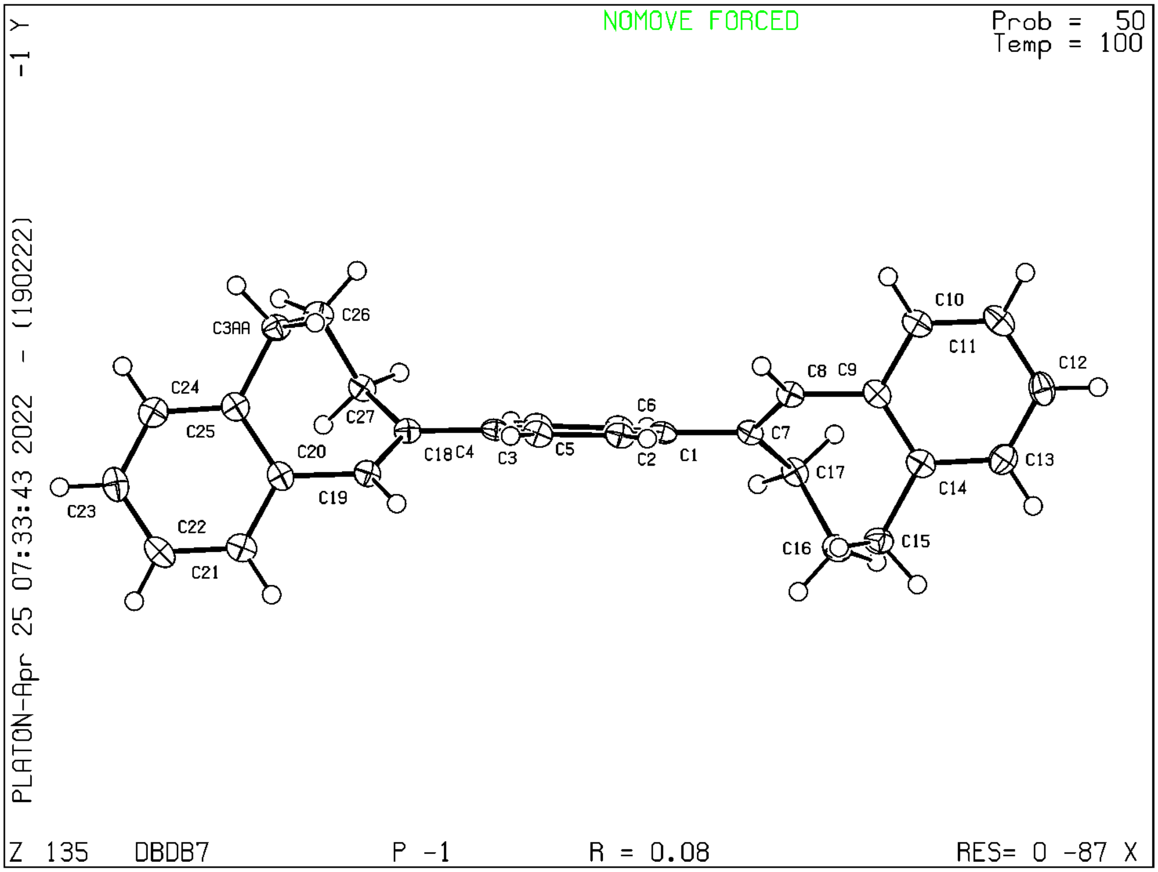
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/02/2022; check.def file version of 19/02/2022

Datablock DBDB7 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: DBDMDB7

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Bond precision:   C-C = 0.0069 A          Wavelength=0.71075

Cell:              a=16.046(8)     b=8.373(4)          c=8.128(4)
                   alpha=90        beta=101.706(6)     gamma=90
Temperature:       123 K

                 Calculated                 Reported
Volume           1069.3(9)                  1069.4(9)
Space group      P 21/c                     P 1 21/c 1
Hall group       -P 2ybc                    -P 2ybc
Moiety formula   C30 H30                    C30 H30
Sum formula      C30 H30                    C30 H30
Mr               390.54                     390.57
Dx,g cm-3        1.213                      1.213
Z                2                          2
Mu (mm-1)        0.068                      0.068
F000             420.0                      420.0
F000'            420.15
h,k,lmax         20,10,10                   20,10,10
Nref             2444                       2428
Tmin,Tmax        0.992,0.993                0.719,0.993
Tmin'            0.990

Correction method= # Reported T Limits: Tmin=0.719 Tmax=0.993
AbsCorr = MULTI-SCAN

Data completeness= 0.993           Theta(max)= 27.433

                                                        wR2(reflections)=
R(reflections)= 0.1138( 1605)                           0.3228( 2428)

S = 1.135                    Npar= 137
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
            The relevant atom site should be identified.
PLAT082_ALERT_2_C High R1 Value .................................       0.11 Report
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..................       0.32 Report
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density      0.58 eA-3
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00688 Ang.
```

Alert level G

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CHEMS02_ALERT_1_G  Please check that you have entered the correct
            _publ_requested_category classification of your compound;
            FI or CI or EI for inorganic; FM or CM or EM for metal-organic;
            FO or CO or EO for organic.
            From the CIF: _publ_requested_category   CHOOSE FI FM FO CI CM CO or A
            From the CIF: _chemical_formula_sum :C30 H30
PLAT012_ALERT_1_G N.O.K.   _shelx_res_checksum Found in CIF ......     Please Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large      0.10 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      5.52 Why ?
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        3.0 Low
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

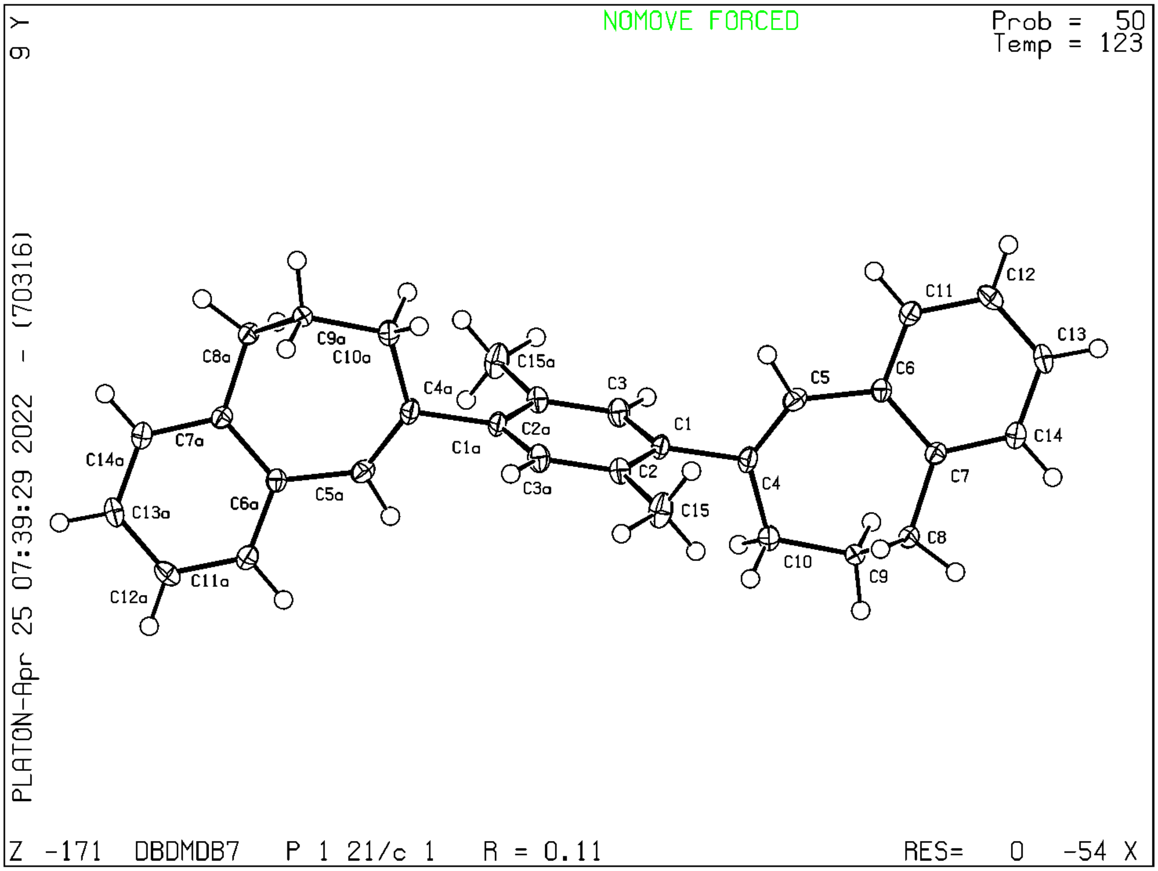
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/02/2022; check.def file version of 19/02/2022

Datablock DBDMDB7 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: DBaMDB7-cross

```
Bond precision:   C-C = 0.0013 A          Wavelength=0.71073

Cell:             a=10.2319(3)     b=11.0510(3)       c=9.6513(3)
                  alpha=90         beta=107.110(3)    gamma=90
Temperature:      120 K

                 Calculated                  Reported
Volume           1043.00(6)                  1043.00(6)
Space group      P 21/c                      P 1 21/c 1
Hall group       -P 2ybc                     -P 2ybc
Moiety formula   C30 H30                     0.4(C30 H30)
Sum formula      C30 H30                     C12 H12
Mr               390.54                      156.22
Dx,g cm-3        1.244                       1.244
Z                2                           5
Mu (mm-1)        0.070                       0.070
F000             420.0                       420.0
F000'            420.15
h,k,lmax         14,15,13                    13,15,13
Nref             3229                        2889
Tmin,Tmax        0.990,0.993                 0.693,1.000
Tmin'            0.990

Correction method= # Reported T Limits: Tmin=0.693 Tmax=1.000
AbsCorr = ANALYTICAL

Data completeness= 0.895          Theta(max)= 30.696

                                                       wR2(reflections)=
R(reflections)= 0.0413( 2703)                          0.1145( 2889)

S = 1.066                  Npar= 137
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

```
 Alert level G
PLAT012_ALERT_1_G N.O.K.   _shelx_res_checksum Found in CIF ......     Please Check
PLAT013_ALERT_1_G N.O.K.   _shelx_hkl_checksum Found in CIF ......     Please Check
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...      0.400 Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........         2.7 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

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Publication of your CIF in other journals

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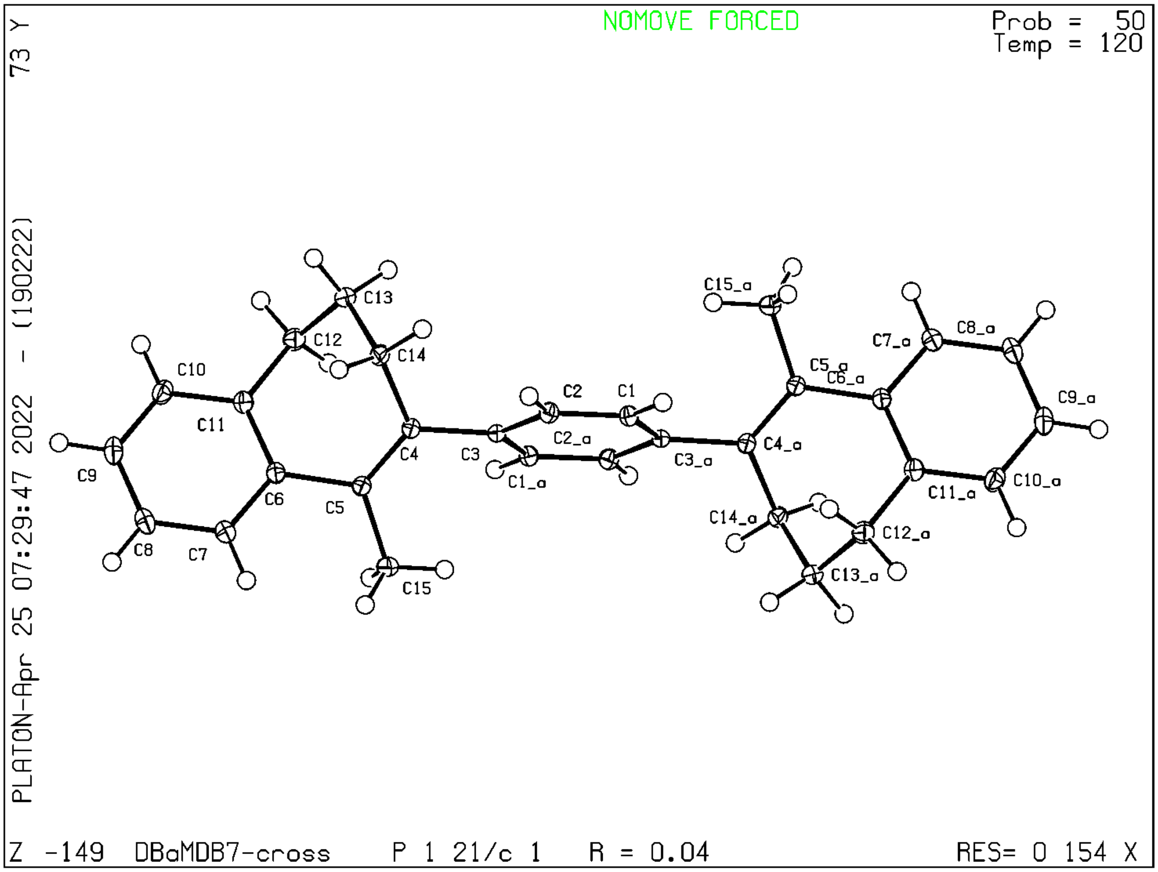
PLATON version of 19/02/2022; check.def file version of 19/02/2022

Datablock DBaMDB7-cross - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: DBaMDB7-parallel

```
Bond precision:   C-C = 0.0019 A           Wavelength=0.71073

Cell:             a=8.3896(4)     b=8.4692(4)          c=15.4856(8)
                  alpha=90        beta=103.274(5)      gamma=90
Temperature:      123 K

                 Calculated                   Reported
Volume           1070.91(9)                   1070.90(9)
Space group      P 21/c                       P 1 21/c 1
Hall group       -P 2ybc                      -P 2ybc
Moiety formula   C30 H30                      0.4(C30 H30)
Sum formula      C30 H30                      C12 H12
Mr               390.54                       156.22
Dx,g cm-3        1.211                        1.211
Z                2                            5
Mu (mm-1)        0.068                        0.068
F000             420.0                        420.0
F000'            420.15
h,k,lmax         12,12,22                     11,12,22
Nref             3351                         2998
Tmin,Tmax        0.990,0.995                  0.640,1.000
Tmin'            0.990

Correction method= # Reported T Limits: Tmin=0.640 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.895           Theta(max)= 30.811

                                                         wR2(reflections)=
R(reflections)= 0.0518( 2531)                            0.1439( 2998)

S = 1.123                  Npar= 137
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

```
   Alert level G
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...      0.400 Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        2.7 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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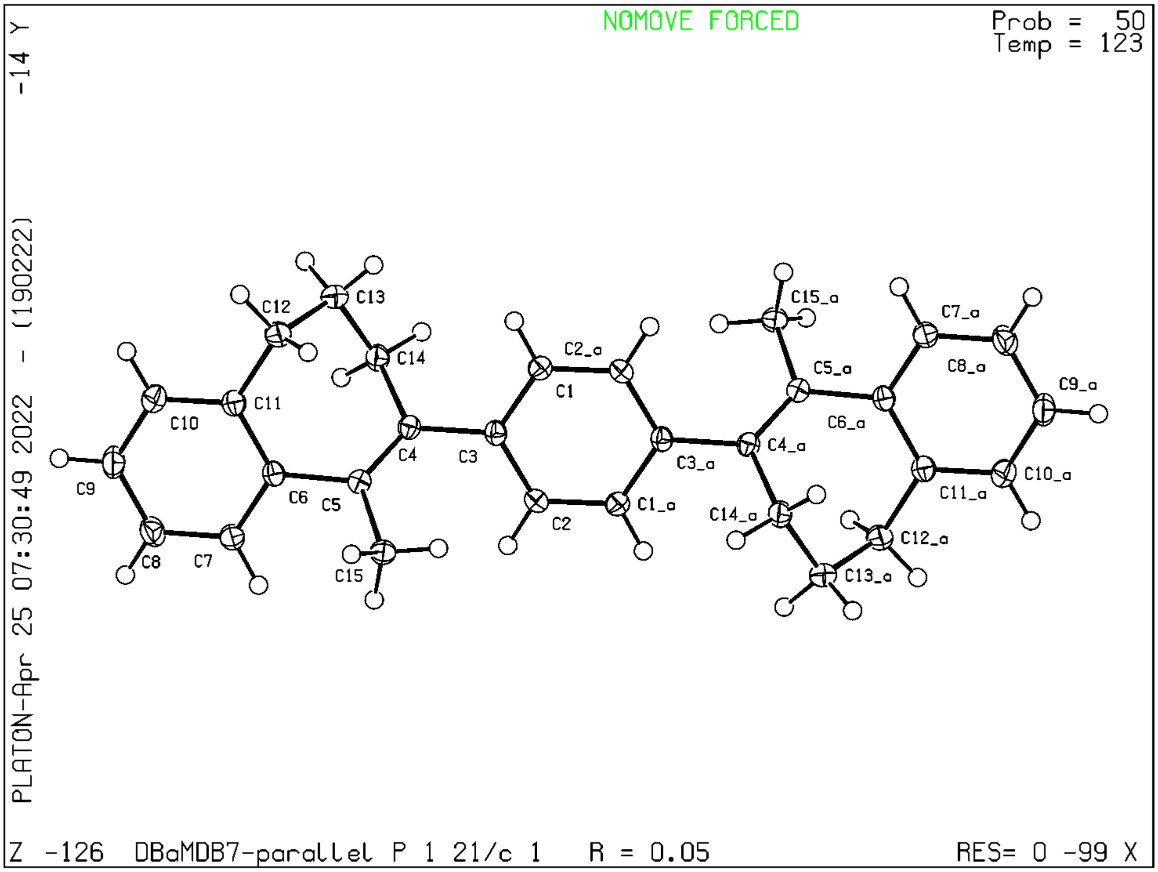
PLATON version of 19/02/2022; check.def file version of 19/02/2022

Datablock DBaMDB7-parallel - ellipsoid plot



checkCIF/PLATON report

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No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: 5DBaMDB7

```
Bond precision:   C-C = 0.0020 A           Wavelength=0.71075

Cell:           a=8.149(3)          b=9.767(4)          c=10.899(4)
                alpha=107.924(3)    beta=105.686(3)     gamma=102.182(5)
Temperature:    123 K

                 Calculated                    Reported
Volume           752.5(5)                      752.5(5)
Space group      P -1                          P -1
Hall group       -P 1                          -P 1
Moiety formula   C40 H50                       C40 H50
Sum formula      C40 H50                       C40 H50
Mr               530.80                        530.83
Dx,g cm-3        1.171                         1.171
Z                1                             1
Mu (mm-1)        0.065                         0.065
F000             290.0                         290.0
F000'            290.10
h,k,lmax         10,12,14                      10,12,14
Nref             3445                          3415
Tmin,Tmax        0.988,0.990                   0.855,0.990
Tmin'            0.988

Correction method= # Reported T Limits: Tmin=0.855 Tmax=0.990
AbsCorr = MULTI-SCAN

Data completeness= 0.991            Theta(max)= 27.469

                                                      wR2(reflections)=
R(reflections)= 0.0451( 2590)                         0.1167( 3415)

S = 1.050                   Npar= 183
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
CHEMS02_ALERT_1_G  Please check that you have entered the correct
            _publ_requested_category classification of your compound;
            FI or CI or EI for inorganic; FM or CM or EM for metal-organic;
            FO or CO or EO for organic.
            From the CIF: _publ_requested_category   CHOOSE FI FM FO CI CM CO or A
            From the CIF: _chemical_formula_sum :C40 H50
PLAT012_ALERT_1_G N.O.K.   _shelx_res_checksum Found in CIF ......     Please Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        3.1 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   3 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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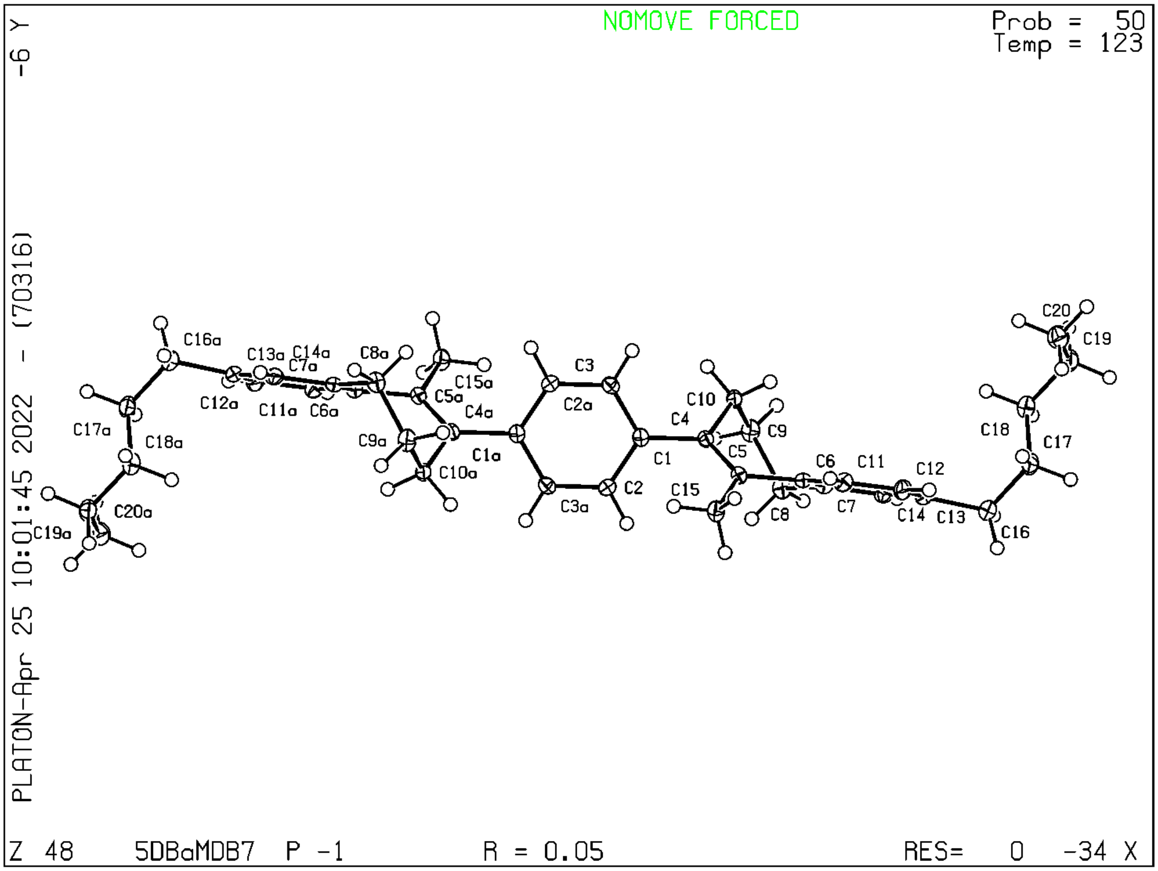
PLATON version of 19/02/2022; check.def file version of 19/02/2022

Datablock 5DBaMDB7 - ellipsoid plot



checkCIF/PLATON report

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No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: tBuDBaMDB7

```
Bond precision:   C-C = 0.0031 A          Wavelength=0.71073

Cell:            a=5.8767(4)       b=6.1160(6)       c=20.3049(14)
                 alpha=93.452(7)   beta=91.590(6)    gamma=93.560(7)
Temperature:     100 K

                  Calculated                    Reported
Volume            726.70(10)                    726.70(10)
Space group       P -1                          P -1
Hall group        -P 1                          -P 1
Moiety formula    C38 H46                       C19 H23
Sum formula       C38 H46                       C19 H23
Mr                502.75                        251.37
Dx,g cm-3         1.149                         1.149
Z                 1                             2
Mu (mm-1)         0.064                         0.064
F000              274.0                         274.0
F000'             274.09
h,k,lmax          8,8,29                        8,8,28
Nref              4664                          3951
Tmin,Tmax         0.989,0.998                   0.654,1.000
Tmin'             0.987

Correction method= # Reported T Limits: Tmin=0.654 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.847           Theta(max)= 31.066

                                                    wR2(reflections)=
R(reflections)= 0.0816( 3172)                       0.2331( 3951)

S = 1.088                    Npar= 176
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
            The relevant atom site should be identified.
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density       0.58 eA-3
```

Alert level G

```
PLAT012_ALERT_1_G N.O.K.   _shelx_res_checksum Found in CIF ......     Please Check
PLAT013_ALERT_1_G N.O.K.   _shelx_hkl_checksum Found in CIF ......     Please Check
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...      0.500 Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.11 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          3 Note
PLAT767_ALERT_4_G INS Embedded LIST 6 Instruction Should be LIST 4     Please Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........         2.6 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   8 ALERT level G = General information/check it is not something unexpected

   5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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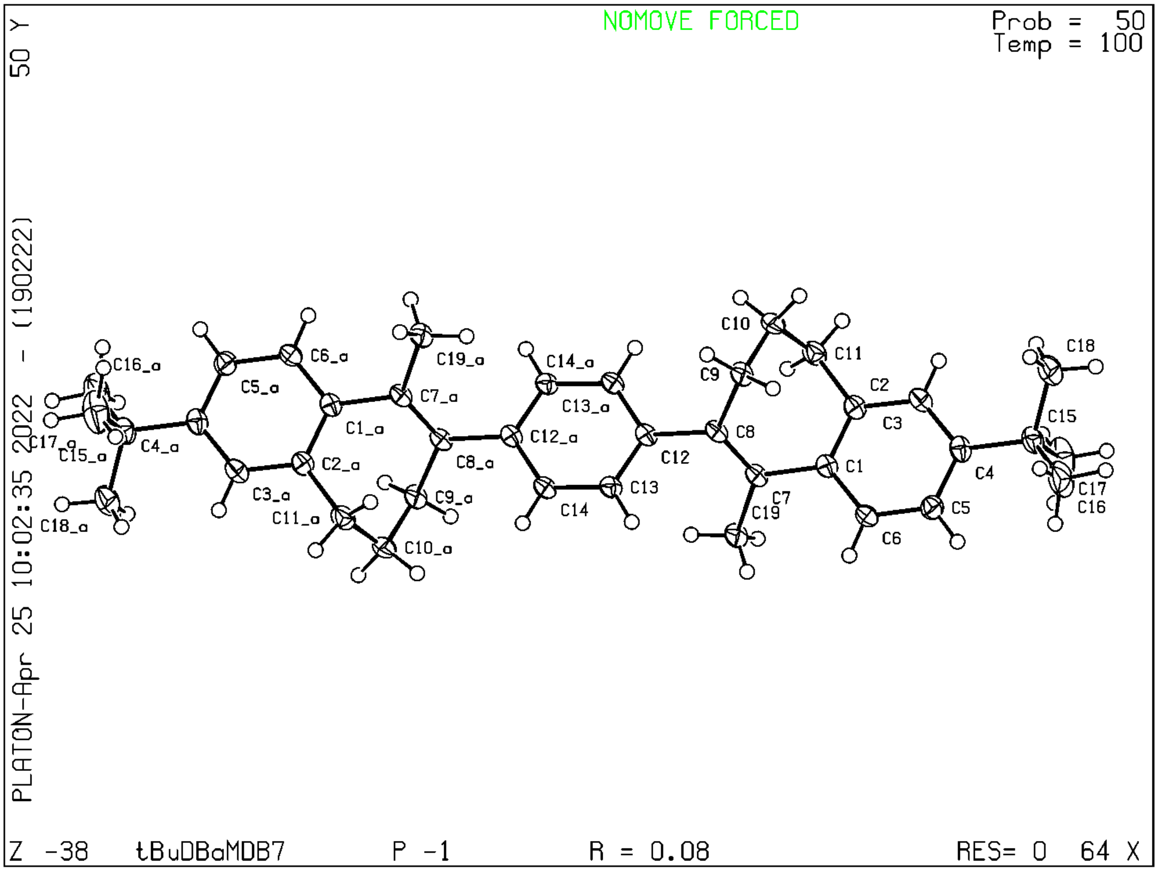
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/02/2022; check.def file version of 19/02/2022

Datablock tBuDBaMDB7 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: dsdmb

```
Bond precision:   C-C = 0.0030 A           Wavelength=0.71073

Cell:             a=11.3650(4)     b=7.0916(3)        c=21.4912(10)
                  alpha=90         beta=98.708(4)     gamma=90
Temperature:      100 K

                 Calculated                  Reported
Volume           1712.14(12)                 1712.14(12)
Space group      P 21/n                      P 1 21/n 1
Hall group       -P 2yn                      -P 2yn
Moiety formula   C24 H22                     C24 H22
Sum formula      C24 H22                     C24 H22
Mr               310.42                      310.41
Dx,g cm-3        1.204                       1.204
Z                4                           4
Mu (mm-1)        0.068                       0.068
F000             664.0                       664.0
F000'            664.24
h,k,lmax         16,10,31                    16,10,31
Nref             5523                        4979
Tmin,Tmax        0.990,0.997                 0.838,1.000
Tmin'            0.990

Correction method= # Reported T Limits: Tmin=0.838 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.902           Theta(max)= 31.119

                                                       wR2(reflections)=
R(reflections)= 0.0821( 4415)                          0.2152( 4979)

S = 1.238                    Npar= 219
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
            The relevant atom site should be identified.
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.02 Report
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density       0.51 eA-3
```

Alert level G

```
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
```

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

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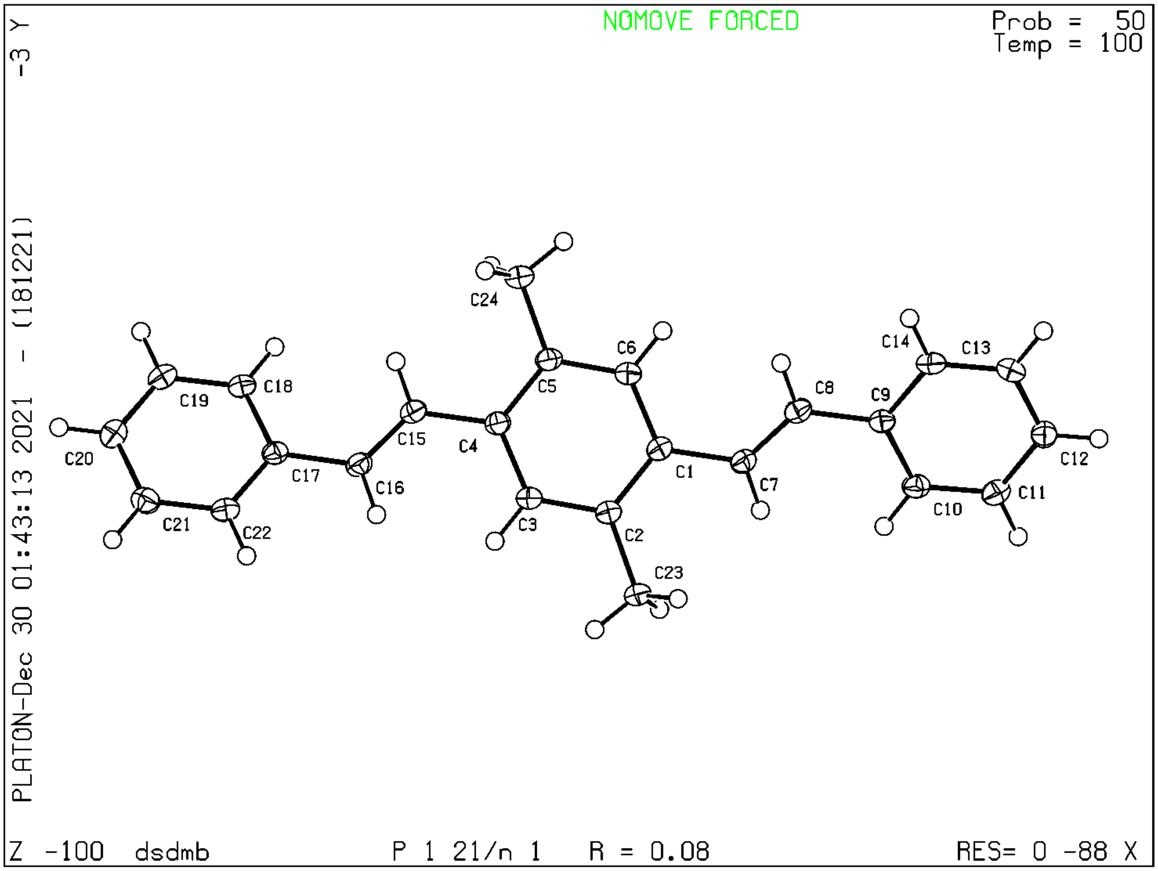
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/12/2021; check.def file version of 18/12/2021

Datablock dsdmb - ellipsoid plot



checkCIF/PLATON report

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No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: DBDB6

```
Bond precision:   C-C = 0.0061 A          Wavelength=0.71073

Cell:              a=6.2540(3)      b=7.5229(5)         c=36.785(3)
                   alpha=90         beta=92.181(6)      gamma=90
Temperature:       100 K

                 Calculated                  Reported
Volume           1729.4(2)                   1729.41(19)
Space group      P 21/c                      P 1 21/c 1
Hall group       -P 2ybc                     -P 2ybc
Moiety formula   C26 H22                     C26 H22
Sum formula      C26 H22                     C26 H22
Mr               334.44                      334.43
Dx,g cm-3        1.285                       1.284
Z                4                           4
Mu (mm-1)        0.072                       0.072
F000             712.0                       712.0
F000'            712.26
h,k,lmax         9,10,53                     9,10,52
Nref             5477                        4496
Tmin,Tmax        0.987,0.998                 0.801,1.000
Tmin'            0.982

Correction method= # Reported T Limits: Tmin=0.801 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.821           Theta(max)= 30.957

                                                          wR2(reflections)=
R(reflections)= 0.1340( 3411)                             0.3409( 4496)

S = 1.197                    Npar= 235
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

```
PLAT211_ALERT_2_A ADP of Atom C17       is N.P.D. or (nearly) 2D .     Please Check
```

Alert level B

```
PLAT097_ALERT_2_B Large Reported Max.  (Positive) Residual Density       0.63 eA-3
```

Alert level C

```
DIFMN02_ALERT_2_C  The minimum difference density is < -0.1*ZMAX*0.75
             _refine_diff_density_min given =     -0.494
            Test value =     -0.450
DIFMN03_ALERT_1_C  The minimum difference density is < -0.1*ZMAX*0.75
            The relevant atom site should be identified.
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
            The relevant atom site should be identified.
PLAT082_ALERT_2_C High R1 Value ..................................       0.13 Report
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ...................       0.34 Report
PLAT098_ALERT_2_C Large Reported Min.  (Negative) Residual Density      -0.49 eA-3
PLAT213_ALERT_2_C Atom C6              has ADP max/min Ratio .....        3.5 oblate
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0061 Ang.
```

Alert level G

```
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      13.22 Why ?
PLAT767_ALERT_4_G INS Embedded LIST 6 Instruction Should be LIST 4     Please Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        2.7 Low
```

```
   1 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
   8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/02/2022; check.def file version of 19/02/2022

Datablock DBDB6 - ellipsoid plot