

## Electronic Supporting Information for

### Exciton coupling in diketopyrrolopyrrole-helicene derivatives leads to red and near-infrared circularly polarized luminescence

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## 1. Experimental procedures

### General method

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at room temperature on an *AVANCE III 400 BRUKER* or an *AVANCE I 500 BRUKER* at Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Chemical shifts  $\delta$  are given in ppm and coupling constants  $J$  in Hz. Chemical shifts for <sup>1</sup>H NMR spectra are referenced relative to residual protium in the deuterated solvent ( $\delta = 7.26$  ppm, CDCl<sub>3</sub>). <sup>13</sup>C shifts are referenced to CDCl<sub>3</sub> peaks at  $\delta = 77.16$  ppm.

High-resolution mass (HR-MS) determinations were performed at CRMPO on a Bruker MaXis 4G by ASAP (+ or -) or ESI with CH<sub>2</sub>Cl<sub>2</sub> as solvent techniques. Experimental and calculated masses are given with consideration of the mass of the electron.

UV-Visible (UV-vis, in M<sup>-1</sup> cm<sup>-1</sup>) absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a FL 920 Edinburgh fluorimeter.

Fluorescence quantum yields  $\Phi$  were measured in diluted solution using the following equation:

$$\frac{\Phi_x}{\Phi_r} = \left( \frac{A_r(\lambda)}{A_x(\lambda)} \right) \left( \frac{n_x^2}{n_r^2} \right) \left( \frac{D_x}{D_r} \right)$$

where:  $A(\lambda)$  is the absorbance at the excitation wavelength  $\lambda$ ,  $n$  is the refractive index,  $D$  is the integrated intensity, and “r” and “x” stand for reference and sample, respectively. The fluorescence quantum yields were measured relative to rhodanine 6G in ethanol ( $\Phi = 0.91$ ) for DPP compounds and to quinine sulfate in 0.5 M sulfuric acid ( $\Phi = 0.59$ ) for **H6(TMS)<sub>2</sub>**.<sup>1,1</sup> Excitation of reference and sample compounds was performed at the same wavelength.

Electrochemical measurements were performed with a potentiostat-galvanostat AutoLab PGSTAT 302N controlled by resident GPES (General Purpose Electrochemical System 4.9) software using a conventional single-compartment three-electrode cell. The working and auxiliary electrodes were platinum electrodes and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 N Bu<sub>4</sub>NPF<sub>6</sub> (tetrabutylammonium hexafluorophosphate) in dichloromethane and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In the experiments, the scan rate was either 100 or 200 mV/s.

Electronic circular dichroism (ECD, in M<sup>-1</sup> cm<sup>-1</sup>) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Biosit - Université de Rennes 1).

The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (see below for a description). The samples were excited using a 90° geometry with a green InGaN (3 mm, 2 V) LED source (Lucky light Electronics Co., LTD,  $\lambda_{\text{max}} = 517$  nm, HWHM = 15 nm). The following parameters were used: emission slit width  $\approx 10$  nm, integration time = 4 sec, scan speed = 60 nm/min, accumulations = 4. The concentration of all the samples was 10<sup>-6</sup> M. The details of the instrument are given in [Zinna, et al., *Chem. Eur. J.*, **2016**, 22, 16089].

Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). Chemicals were purchased from Sigma-Aldrich, Alfa Aesar or TCI Europe and used as received.

## Synthetic procedures

*P*- and *M*-2,15-bis((trimethylsilyl)ethynyl)[6]helicene (*P*- and *M*-**H6(TMS)<sub>2</sub>**), 3-(5-bromothiophen-2-yl)-2,5-dioctyl-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**DPPBr**), and 3-(5-bromothiophen-2-yl)-2,5-dioctyl-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**DPPBr<sub>2</sub>**) were prepared using previously reported procedures.<sup>1,2,1,3</sup>

### Synthetic procedure for **H6DPP** and **H6(DPP)<sub>2</sub>**

Enantiopure *P*- or *M*-**H6(TMS)<sub>2</sub>** (75 mg, 0.14 mmol) was dissolved in CHCl<sub>3</sub> (5 mL). Tetra-*n*-butylammonium fluoride (1.0 M solution in THF) was added dropwise to the stirred solution until an optimal product mixture was reached, mainly composed of the mono- and fully deprotected hexahelicene derivatives (the progress of the reaction was carefully monitored by TLC after addition of each 15 drops of TBAF solution). Then, the reaction was quenched with CH<sub>3</sub>COOH (0.1 mL, 1.7 mmol) and the mixture immediately passed through a short plug of silica gel (CH<sub>2</sub>Cl<sub>2</sub>). The mono- (*P*- and *M*-**H6a**) and fully deprotected (*P*- and *M*-**H6b**) hexahelicene derivatives mixture was directly used in the next steps without further purification.

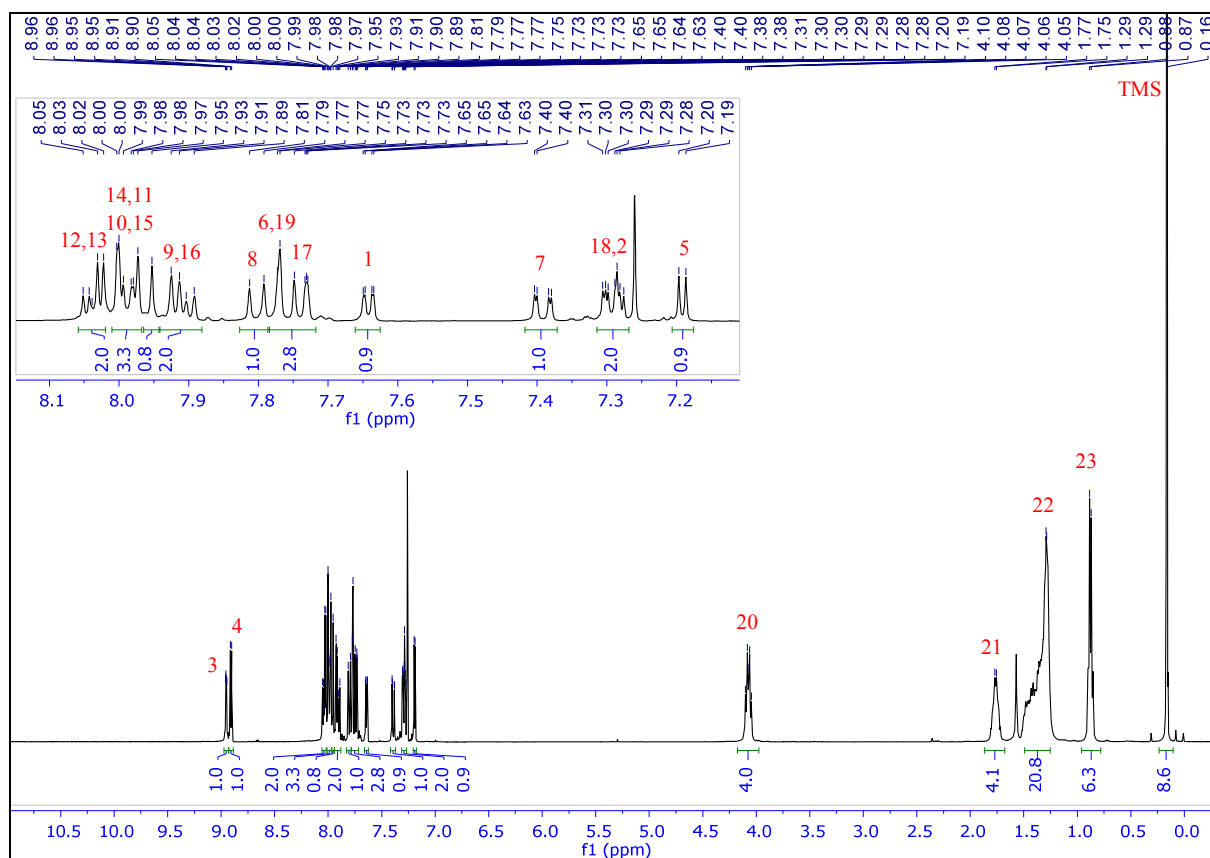
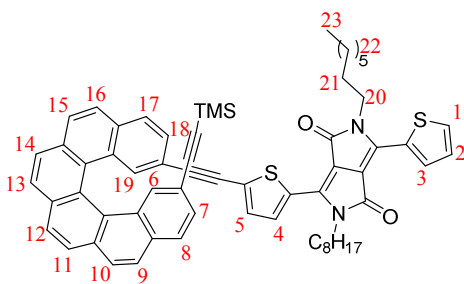
The mixture of *P*- and *M*-**H6a** or *P*- and *M*-**H6b** and **DPPBr** (347 mg, 0.58 mmol) was placed in an oven-dried flask of 25 mL under argon. Then 7 mL of dry toluene and 3 mL of dry Et<sub>3</sub>N were added and the resulting solution was freed from oxygen by three freeze-pump-thaw cycles. Pd(PPh<sub>3</sub>)<sub>4</sub> (17 mg, 0.01 mmol) and CuI (5.5 mg, 0.03 mmol) were added and the solution was refluxed for 3 hours. After cooling down to room temperature, the solution was passed through a short silica plug (CH<sub>2</sub>Cl<sub>2</sub>). The crude mixture was further purified by column chromatography (toluene/CHCl<sub>3</sub>: 100/0 to 95/5) and size-exclusion chromatography (BioBeads SX-2, CHCl<sub>3</sub>) before precipitated using CHCl<sub>3</sub>/MeOH to yield *P*- and *M*-**H6DPP** (32 mg, 70%) or *P*- and *M*-**H6(DPP)<sub>2</sub>** (51 mg, 75%) as dark red solids.

### **H6DPP**

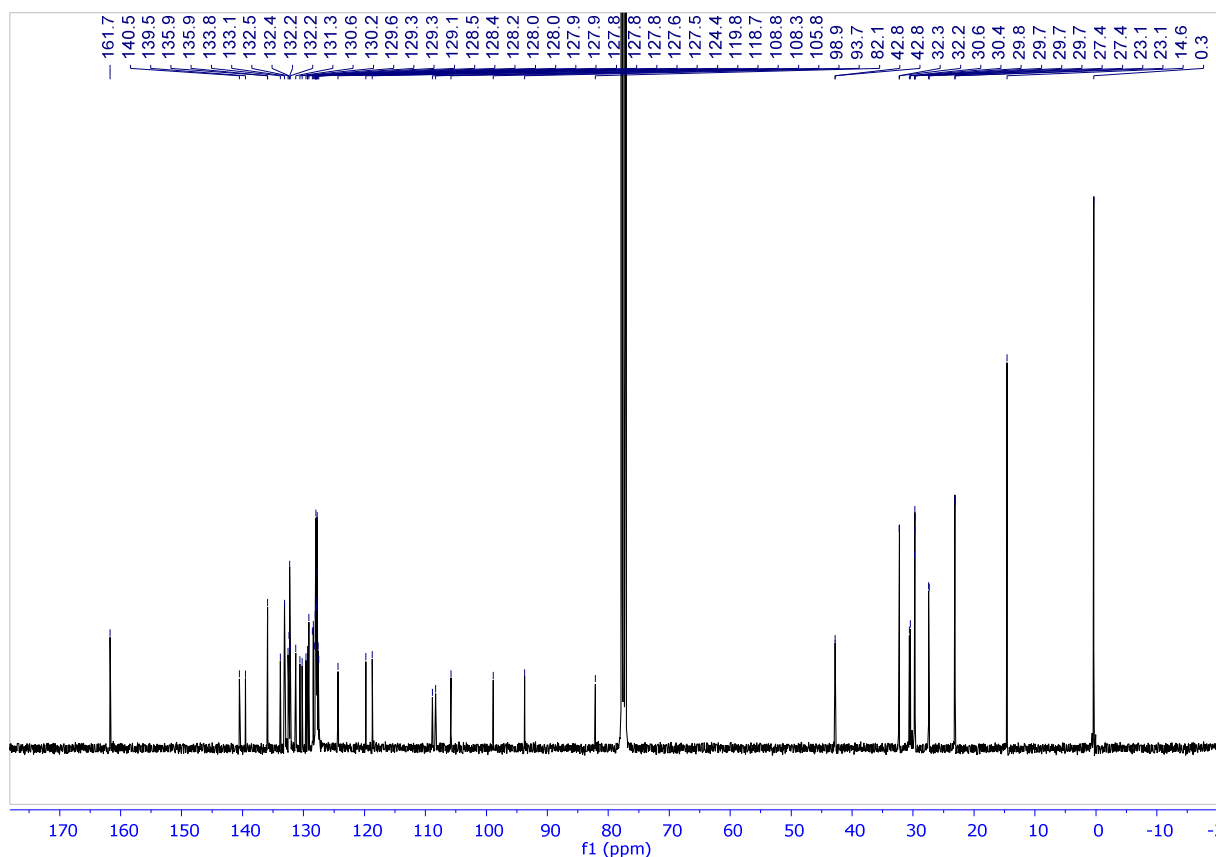
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.95 (dd, *J* = 3.9, 1.1 Hz, 1H), 8.91 (d, *J* = 4.2 Hz, 1H), 8.06-8.01 (m, 2H), 8.01-7.96 (m, 3H), 7.95 (bs, 1H), 7.93-7.89 (m, 2H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.78-7.72 (m, 3H), 7.64 (dd, *J* = 4.0 Hz, 1.2 Hz, 1H), 7.39 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.31-7.29 (m, 1H), 7.29-7.27 (m, 1H), 7.19 (d, *J* = 4.1 Hz, 1H), 4.07 (q, *J* = 6.9 Hz, 4H), 1.82-1.70 (m, 4H), 1.53-1.20, (m, 22H), 0.93-0.82 (m, 6H), 0.17-0.15 (m, 9H).

<sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 161.7, 140.5, 139.5, 135.9, 135.9, 133.8, 133.1, 132.5, 132.4, 132.3, 132.2, 131.3, 130.6, 130.2, 129.6, 129.4, 129.3, 129.1, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 127.5, 124.4, 119.8, 118.7, 108.8, 108.3, 105.8, 98.9, 93.8, 82.1, 42.8, 42.8, 32.3, 32.3, 30.6, 30.4, 29.8, 29.7, 29.7, 29.7, 27.4, 27.4, 23.1, 23.1, 14.6, 0.3.

HR-MS Bruker MaXis 4G, ASAP (+), 360°C; ion [M+H]<sup>+</sup>, C<sub>63</sub>H<sub>63</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>, m/z calculated 971.40948, m/z experimental 971.4089 (Δ=1 ppm).



**Figure S1.1.**  $^1\text{H}$  NMR spectrum of **H6DPP** in  $\text{CDCl}_3$  at 298 K (400 MHz).



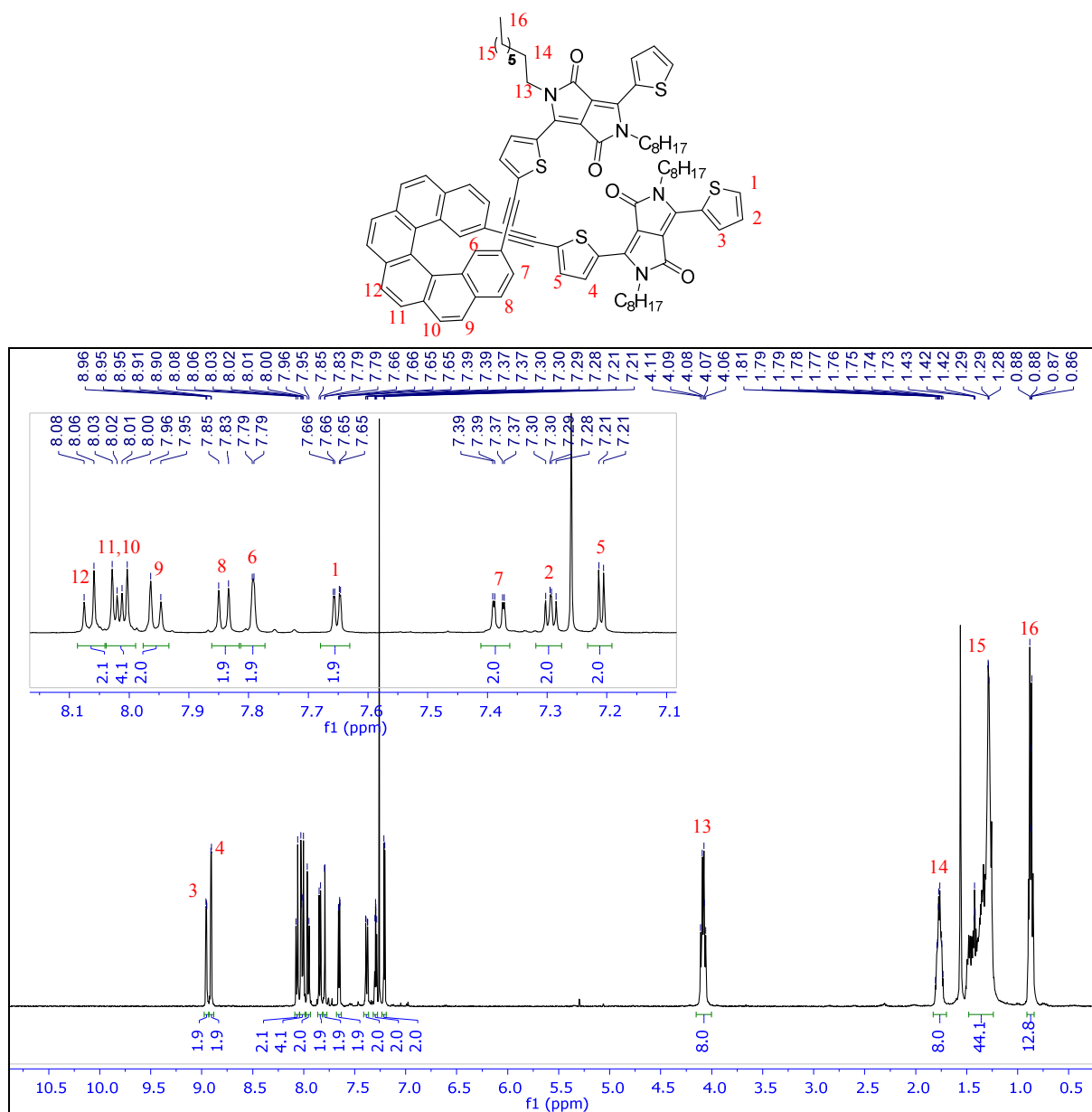
**Figure S1.2.**  $^{13}\text{C}$  NMR spectrum of **H6DPP** in  $\text{CDCl}_3$  at 298 K (100 MHz).

### **H6(DPP)<sub>2</sub>**

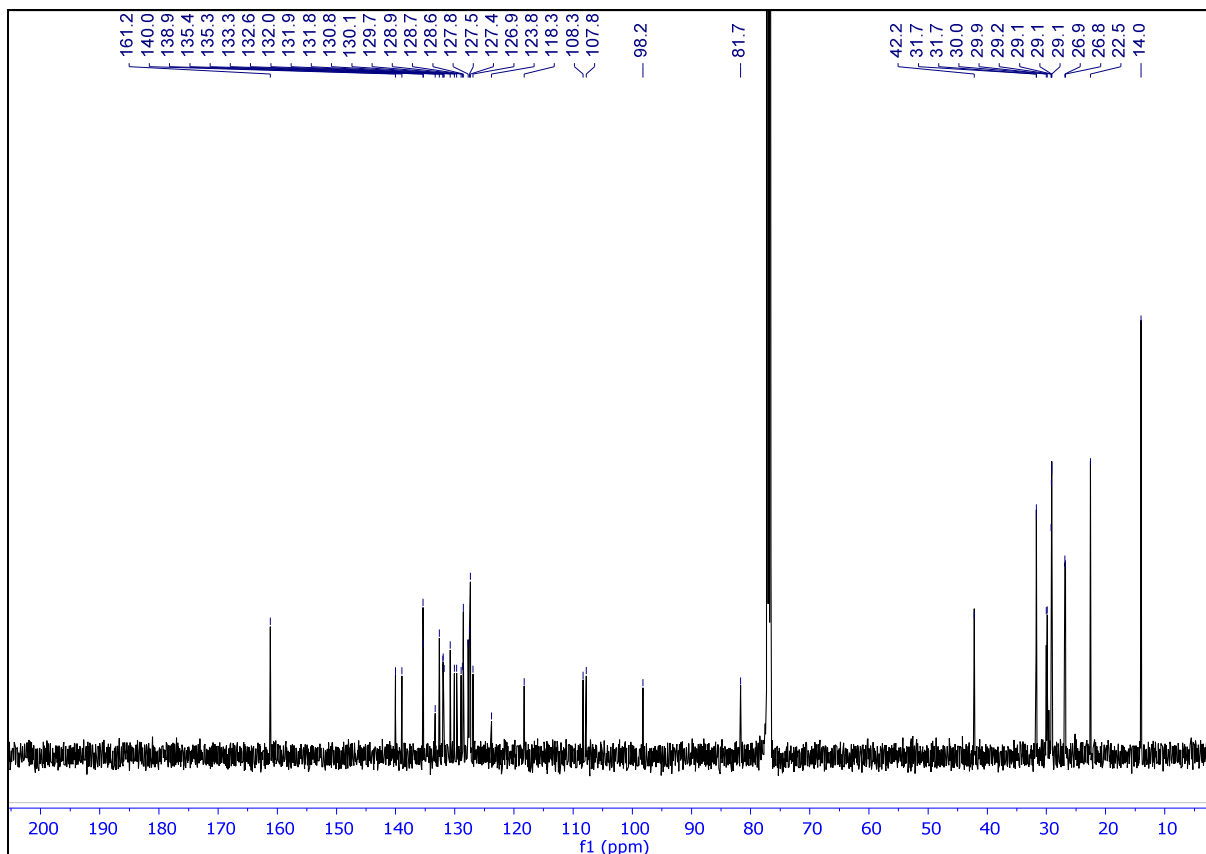
**$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)**  $\delta$  8.95 (dd,  $J = 3.9, 1.1$  Hz, 2H), 8.91 (d,  $J = 4.1$  Hz, 2H), 8.07 (d,  $J = 8.2$  Hz, 2H), 8.02 (d,  $J = 8.2$  Hz, 2H), 8.01 (d,  $J = 8.6$  Hz, 2H), 7.96 (d,  $J = 8.6$  Hz, 2H), 7.84 (d,  $J = 8.3$  Hz, 2H), 7.79 (m, 2H), 7.65 (dd,  $J = 5.0$  Hz and 1.1 Hz, 2H), 7.38 (dd,  $J = 8.2$  Hz and 1.6 Hz, 2H), 7.30 (m, 2H), 7.21 (d,  $J = 4.1$  Hz, 2H), 4.08 (q,  $J = 8.6$  Hz, 9H), 1.79 – 1.73 (m, 8H), 1.50 – 1.23 (m, 40H), 0.90 – 0.82 (m, 12H).

**$^{13}\text{C}$  NMR (125 MHz, Chloroform-*d*)**  $\delta$  161.2, 140.0, 138.9, 135.4, 135.3, 133.3, 132.6, 132.0, 131.9, 131.8, 130.8, 130.1, 129.7, 129.0, 128.7, 128.6, 127.8, 127.5, 127.4, 126.9, 123.8, 118.3, 108.3, 107.8, 98.2, 81.7, 42.2, 31.7, 31.7, 30.0, 29.9, 29.2, 29.2, 29.1, 29.1, 26.9, 26.8, 22.5, 14.0.

**HR-MS** Thermo-Fisher Q-Exactive, ESI (+),  $\text{CH}_2\text{Cl}_2$ ; ion  $[\text{M}]^+$ ;  $\text{C}_{90}\text{H}_{92}\text{N}_4\text{O}_4\text{S}_4$ ,  $m/z$  calculated 1420.60015,  $m/z$  experimental 1420.5994 ( $\Delta=0$  ppm).



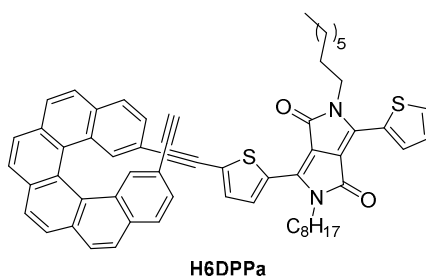
**Figure S1.3.**  $^1\text{H NMR}$  spectrum of  $\text{H6(DPP)}_2$  in  $\text{CDCl}_3$  at 298 K (500 MHz).



**Figure S1.4.**  $^{13}\text{C}$  NMR spectrum of **H6(DPP)<sub>2</sub>** in  $\text{CDCl}_3$  at 298 K (125 MHz).

#### Synthetic procedure for **DPP(H6DPP)<sub>2</sub>**

Enantiopure *P*- or *M*-**H6DPP** (20 mg, 0.02 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL). Tetra-*n*-butylammonium fluoride (0.1 mL, 1.0 M solution in THF) was added dropwise and the resulting solution was stirred for 0.5 hour. Then, the mixture was passed through a short plug of silica gel ( $\text{CH}_2\text{Cl}_2$ ) to afford deprotected *P*- or *M*-**H6DPPa** which was directly used in the next step without further purification.



*P*- or *M*-**H6DPPa** (18 mg, 0.02 mmol) and **DPPBr<sub>2</sub>** (6.2 mg, 9.3  $\mu\text{mol}$ ) were placed in an oven-dried flask of 25 mL under argon. Then 7 mL of dry toluene and 3 mL of dry  $\text{Et}_3\text{N}$  were added and the resulting solution was freed from oxygen by three freeze-pump-thaw cycles.  $\text{Pd}(\text{PPh}_3)_4$  (2.4 mg, 0.2  $\mu\text{mol}$ ) and  $\text{CuI}$  (1.0 mg, 0.4  $\mu\text{mol}$ ) were added and the solution was refluxed for 3 hours. After cooling down to room temperature, the solution was passed

through a short silica plug (CH<sub>2</sub>Cl<sub>2</sub>). The crude mixture was further purified by column chromatography (CHCl<sub>3</sub>) and size-exclusion chromatography (BioBeads SX-2, CHCl<sub>3</sub>) before precipitated using CHCl<sub>3</sub>/MeOH to yield *P*- and *M*-**DPP(H6DPP)**<sub>2</sub> (respectively 11 and 14 mg, 50 and 65%).

**<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)** δ 8.96 (dd, *J* = 3.9, 1.1 Hz, 2H), 8.94 (d, *J* = 4.1 Hz, 2H), 8.91 (d, *J* = 4.1 Hz, 2H), 8.09 – 8.03 (m, 7H), 8.03 – 7.99 (m, 7H), 7.99 – 7.94 (m, 4H), 7.85 (dd, *J* = 8.3, 2.0 Hz, 4H), 7.80 – 7.78 (m, 2H), 7.66 (dd, *J* = 5.0, 1.2 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.30 (dd, *J* = 5.0, 3.9 Hz, 2H), 7.22 (m, 4H), 4.16 – 4.04 (m, 12H), 1.84 – 1.70 (m, 12H), 1.52 – 1.17 (m, 60H), 0.94 – 0.79 (m, 18H).

**<sup>13</sup>C NMR (125 MHz, Chloroform-*d*)** δ 161.4, 161.3, 140.3, 139.2, 139.2, 135.8, 135.6, 135.6, 133.6, 132.9, 132.8, 132.4, 132.3, 132.2, 132.1, 131.0, 130.3, 130.20, 129.9, 129.2, 129.0, 128.8, 128.0, 127.8, 127.8, 127.6, 127.2, 127.1, 124.0, 118.5, 108.8, 108.6, 108.0, 98.7, 98.4, 82.0, 81.9, 77.4, 42.6, 42.5, 32.0, 31.9, 30.3, 30.1, 29.9, 29.6, 29.5, 29.4, 29.3, 27.2, 27.1, 27.0, 22.9, 22.8, 14.3.

**HR-MS** Thermo-Fisher Q-Exactive, ESI (+), CH<sub>2</sub>Cl<sub>2</sub>; ion [M]<sup>+</sup>, C<sub>150</sub>H<sub>144</sub>N<sub>6</sub>O<sub>6</sub>S<sub>6</sub>, *m/z* calculated 2316.94662, *m/z* experimental 2316.9409 (Δ=2 ppm).



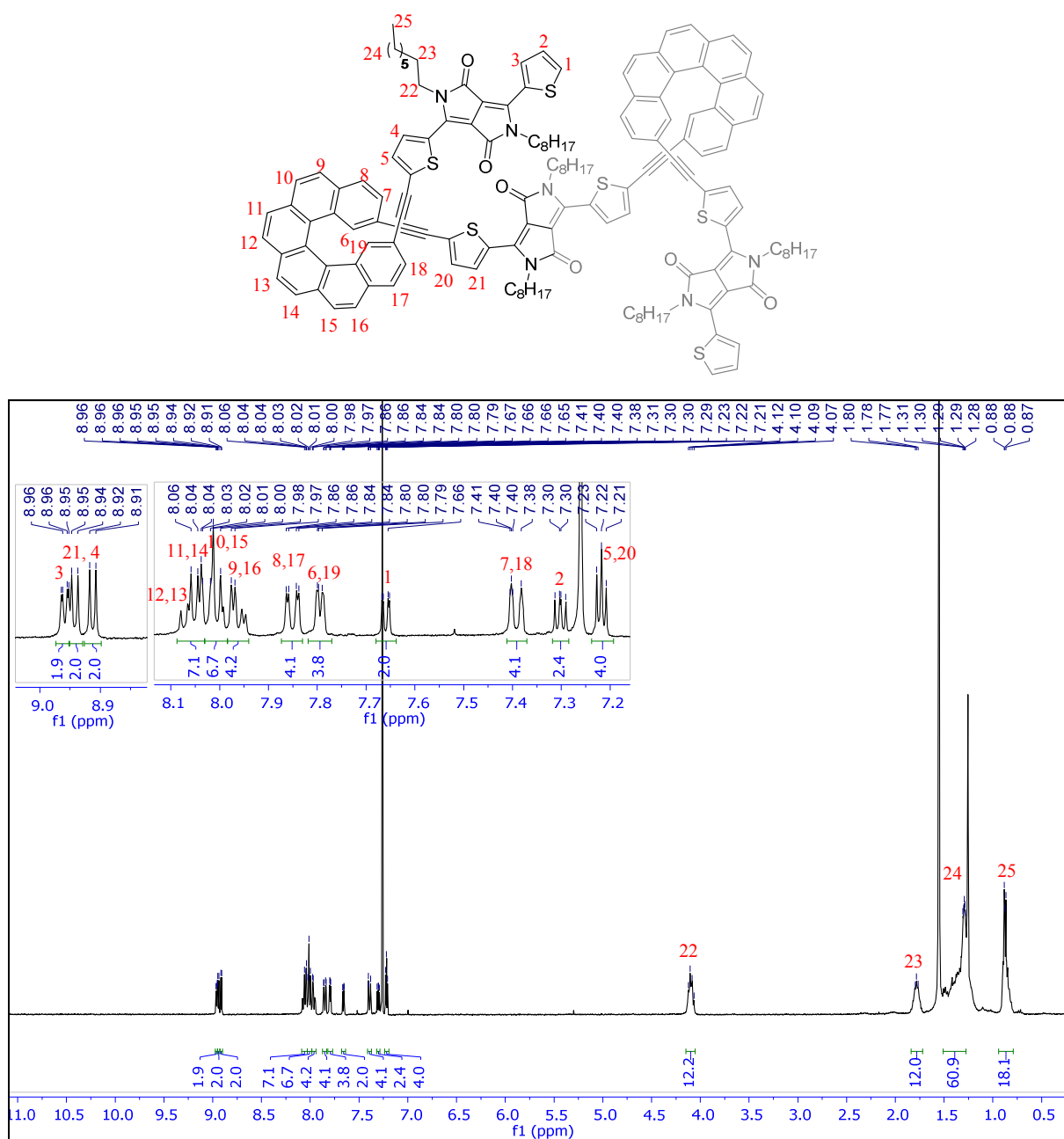


Figure S1.5.  $^1\text{H}$  NMR spectrum of  $\text{DPP}(\text{H6DPP})_2$  in  $\text{CDCl}_3$  at 298 K (400 MHz).

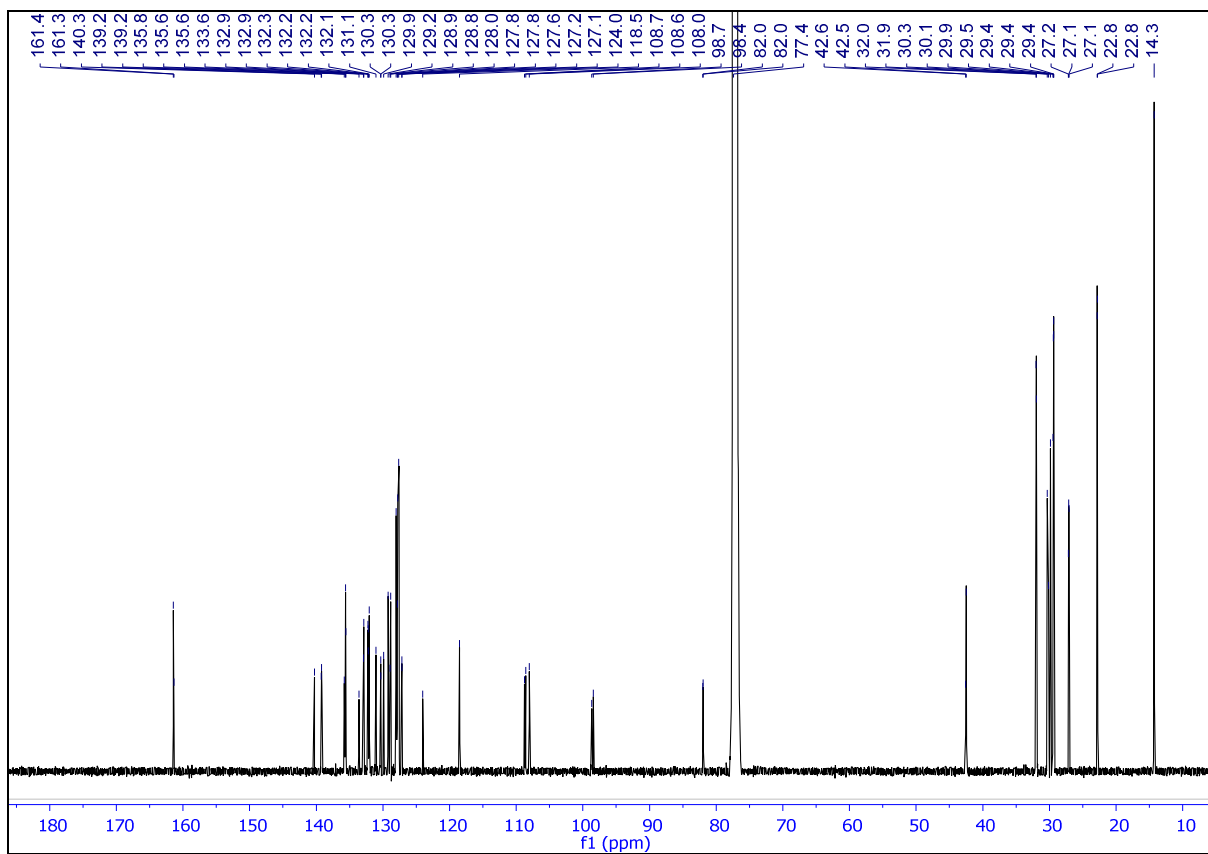
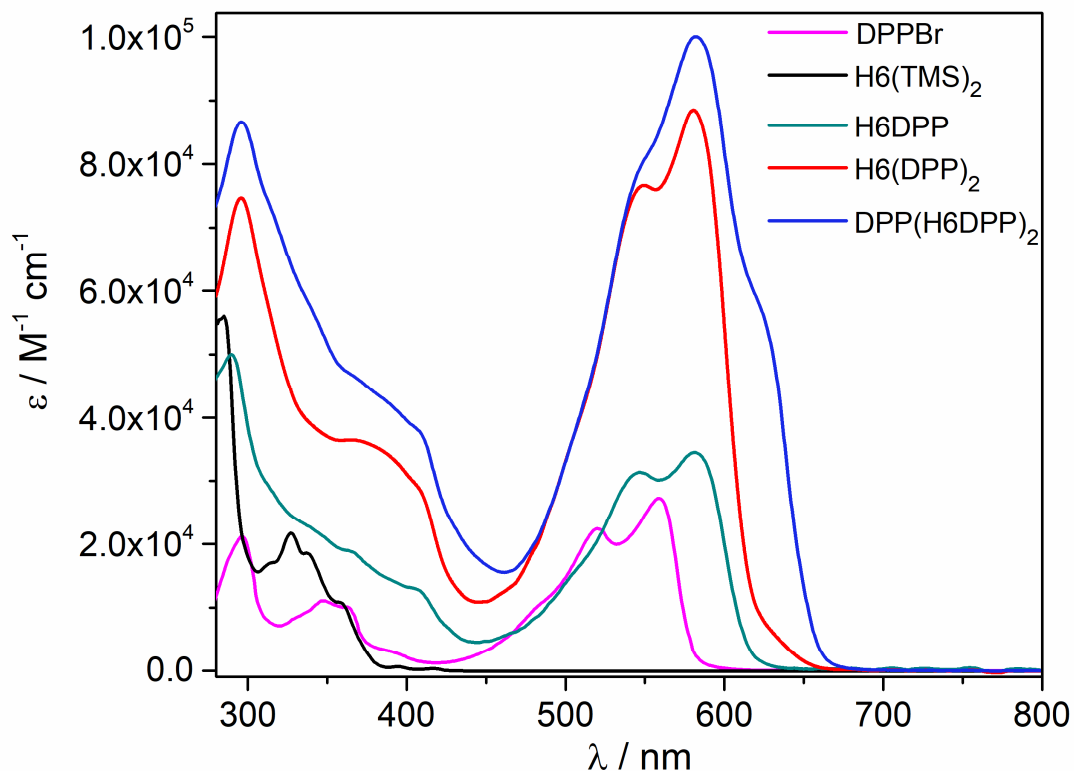
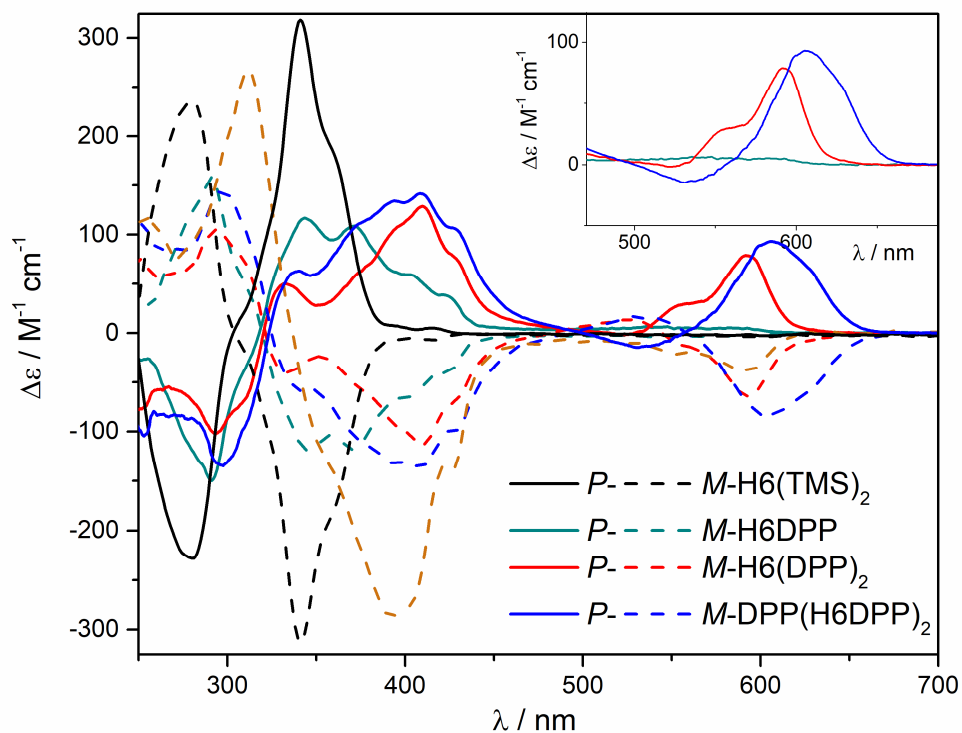


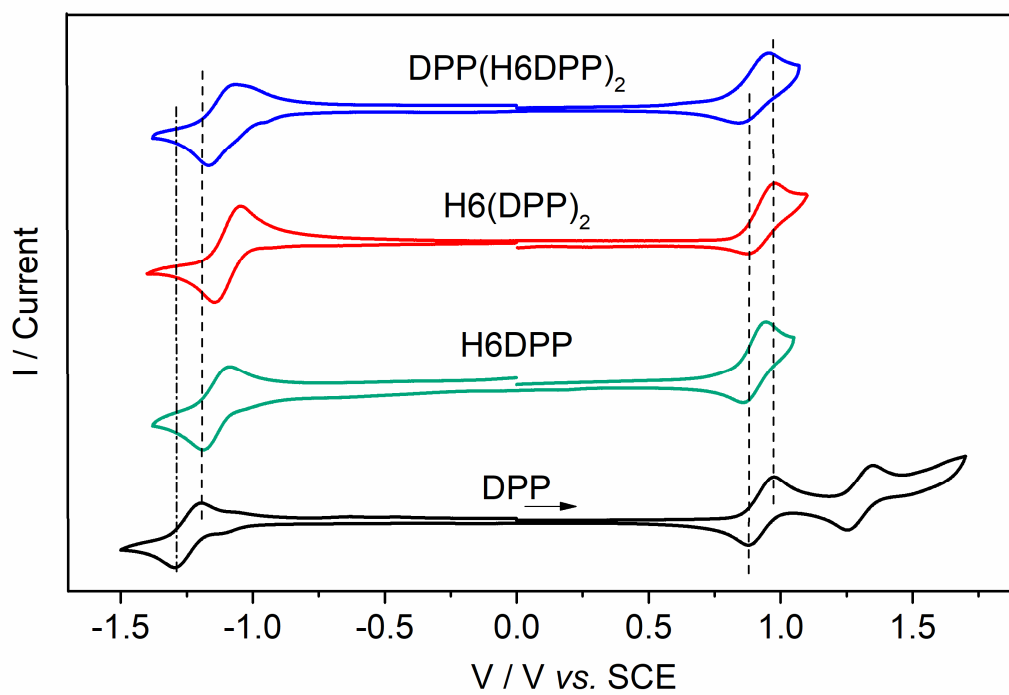
Figure S1.6.  $^{13}\text{C}$  NMR spectrum of **DPP(H6DPP)<sub>2</sub>** in  $\text{CDCl}_3$  at 298 K (125 MHz).



**Figure S1.7.** UVvis spectra of **H6(TMS)<sub>2</sub>** (black), **DPPBr** (purple), **H6DPP** (green), **H6(DPP)<sub>2</sub>** (red) and **DPP(H6DPP)<sub>2</sub>** (blue) compounds in dichloromethane solution at 298 K ( $\sim 10^{-5}$  M).

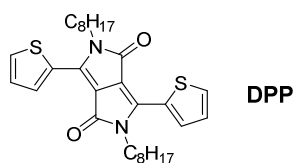


**Figure S1.8.** ECD spectra of *P* (solid lines) and *M* (dash lines) enantiopure **H6(TMS)<sub>2</sub>** (black), **H6DPP** (green), **H6(DPP)<sub>2</sub>** (red) and **DPP(H6DPP)<sub>2</sub>** (blue) compounds in dichloromethane solution at 298 K ( $\sim 10^{-5}$  M).



**Figure S1.9.** Cyclic voltammogram of **DPP**, **H6DPP**, **H6(DPP)<sub>2</sub>**, and **DPP(H6DPP)<sub>2</sub>** versus saturated calomel electrode (SCE) as the reference and 0.1 M  $\text{Bu}_4\text{NPF}_6$  in dichloromethane as the electrolyte.

**Table S1.1.** Redox potentials ( $E_{\text{Ox}}$  and  $E_{\text{Red}}$ ) of **DPP**, **H6DPP**, **H6(DPP)<sub>2</sub>**, and **DPP(H6DPP)<sub>2</sub>**, referenced *versus* saturated calomel electrode (SCE) and given in V. Here **DPP** refers to 2,5-dioctyl-3,6-di-2-thienyl-pyrrolo[3,4-c]pyrrole-1,4-dione.<sup>1,4</sup>



Compound	$E_{\text{Ox}}$ DPP <sup>+0</sup>	$E_{\text{Red}}$ DPP <sup>0/-</sup>	HOMO <sup>a</sup> (eV)	LUMO <sup>b</sup> (eV)	$E_g^c$ (eV)
<b>DPP</b>	0.93	-1.25	-5.67	-3.49	2.18
<b>H6DPP</b>	0.90	-1.14	-5.64	-3.60	2.04
<b>H6DPP<sub>2</sub></b>	0.93	-1.10	-5.67	-3.64	2.03
<b>DPP(H6DPP)<sub>2</sub></b>	0.90	-1.12	-5.64	-3.62	2.02

<sup>a</sup> HOMO energy levels estimated from electrochemical results using the following equation:<sup>1,5</sup>

$$\text{HOMO} = -(E_{\text{Ox}} + 4.74) \text{ eV}$$

<sup>b</sup> LUMO energy levels estimated from electrochemical results using the following equation:<sup>1,5</sup>

$$\text{LUMO} = -(E_{\text{Red}} + 4.74) \text{ eV}$$

<sup>c</sup> energy gaps ( $E_g$ ) values estimated from the difference between LUMO and HOMO energy levels

**Table S1.2.** Quantum yields (averaged values) of fluorescence for the reported compounds.

Compound	$\phi_{\text{ave}}$
<b>H6(TMS)<sub>2</sub></b>	0.07 <sup>a</sup>
<b>H6DPP</b>	0.39 <sup>b</sup>
<b>H6(DPP)<sub>2</sub></b>	0.41 <sup>b</sup>
<b>DPP(H6DPP)<sub>2</sub></b>	0.35 <sup>b</sup>

<sup>a</sup> relative to quinine sulfate in 0.5 M sulphuric acid

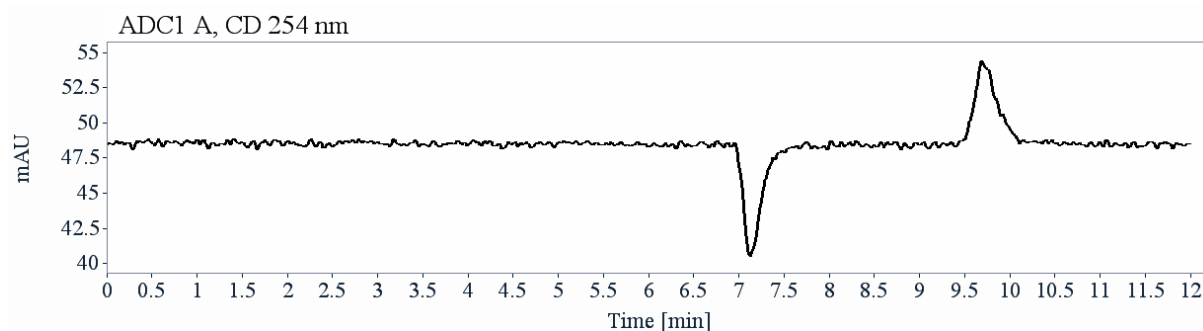
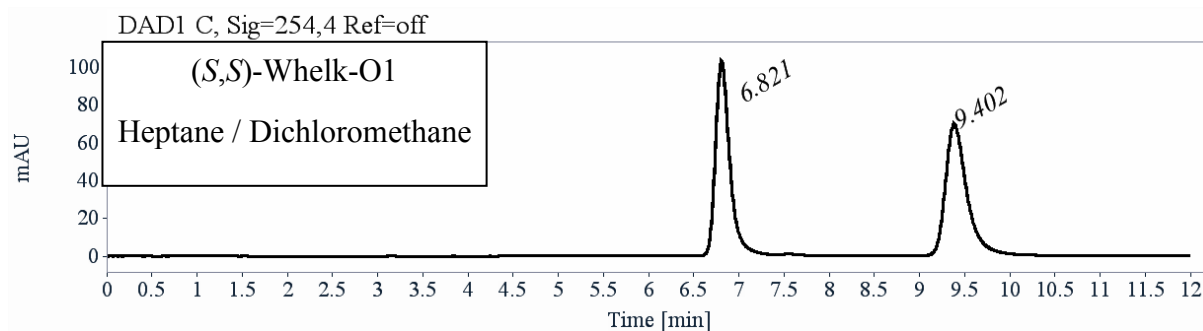
<sup>b</sup> relative to rhodanine 6G in ethanol

## HPLC separations

### - Analytical chiral HPLC separation for $H_6(TMS)_2$

• The sample is dissolved in chloroform, injected on the chiral column, and detected with an UV detector at 254 nm and with circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	$\alpha$	Rs
(S,S)-Whelk-O1	Heptane / Dichloromethane 90/10	6.82 (-)	1.31	9.40 (+)	2.19	1.67	7.56



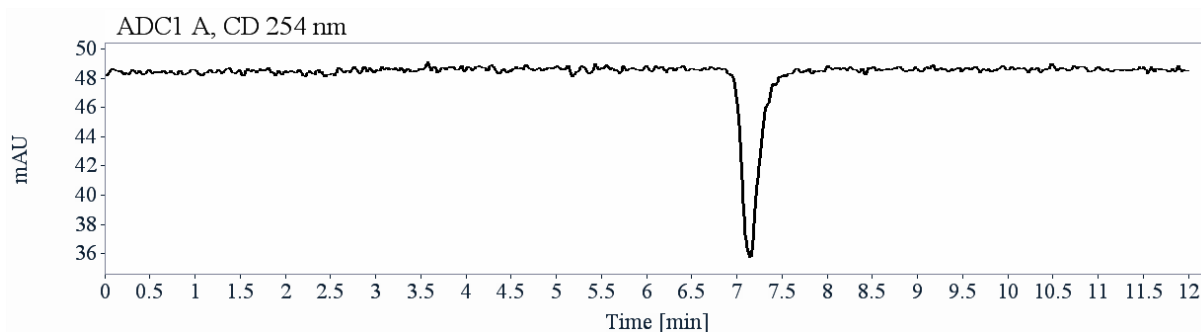
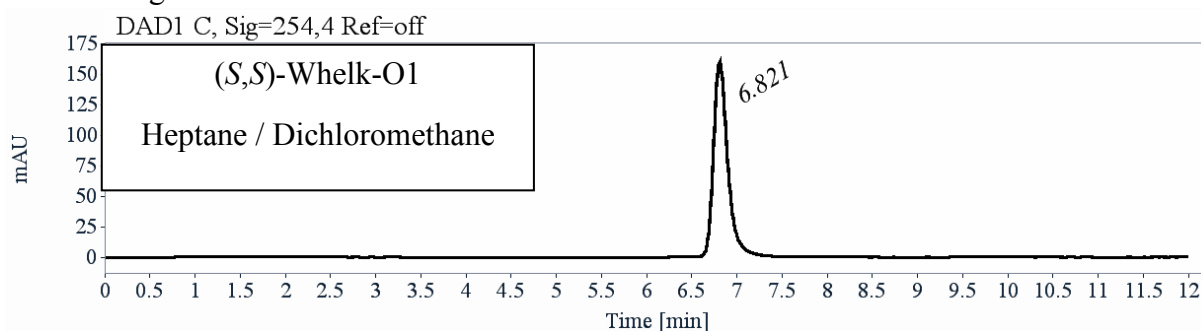
**Signal:** DAD1 C, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.82	1132	49.98	1.31		
9.40	1134	50.02	2.19	1.67	7.56
Sum	2266	100.00			

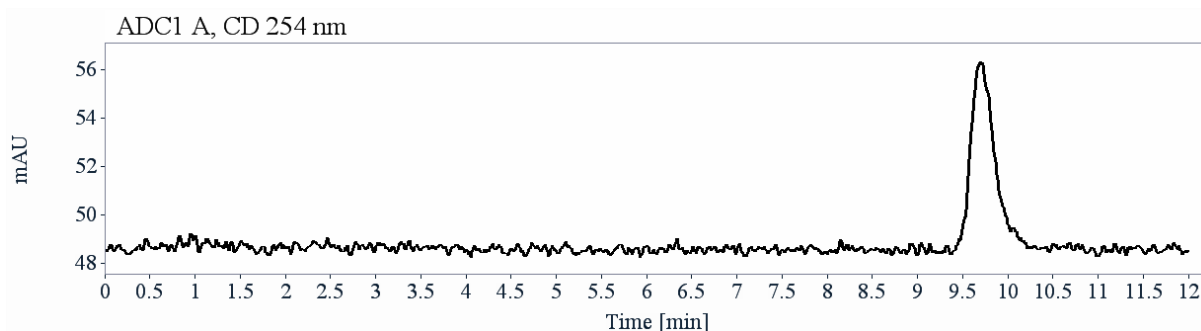
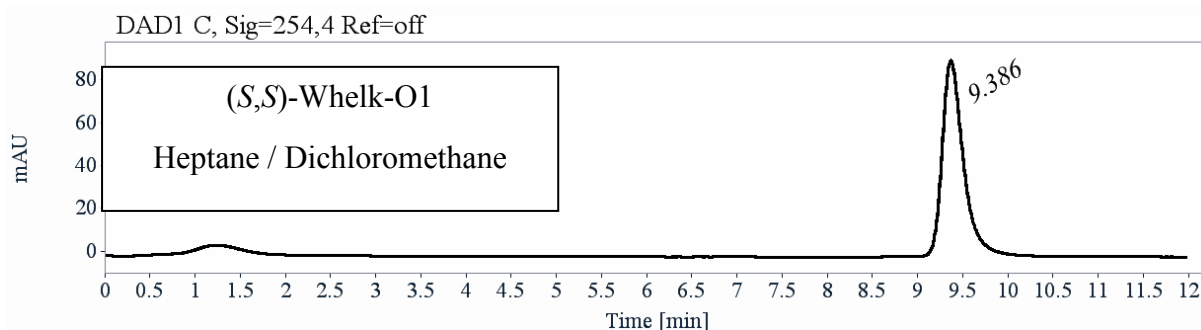
### - Semi-preparative separation for compound $H_6(TMS)_2$

- Sample preparation: About 445 mg of  $H_6(TMS)_2$  are dissolved in 30 mL of a mixture hexane/ dichloromethane (87/13).
- Chromatographic conditions: (S,S)-Whelk-O1 (250 x 10 mm), hexane / dichloromethane (90/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 220 nm.
- Injections (stacked): times 300  $\mu$ L, every 4.8 minutes.
- First fraction: 199 mg of the first eluted ((-, CD 254nm)-enantiomer) with ee > 99.5%

- Second fraction: 205 mg of the second eluted ((+, CD 254nm)-enantiomer) with ee > 99.5%
- Chromatograms of the collected fractions:



RT [min]	Area	Area%
6.82	1746	100.00
Sum	1746	100.00

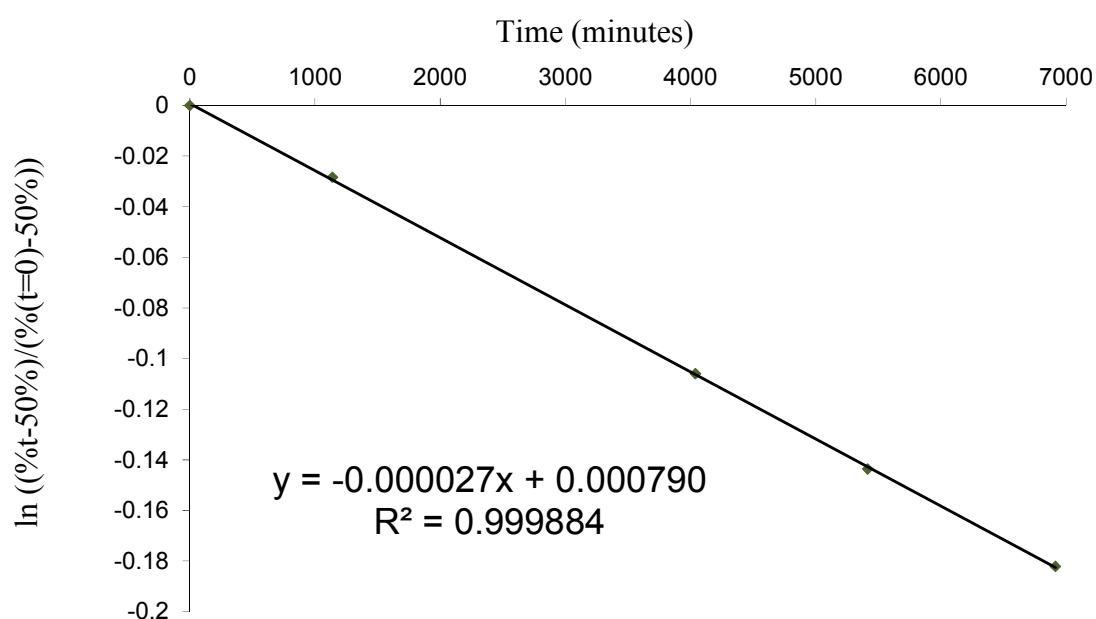


RT [min]	Area	Area%
9.39	1477	100.00
Sum	1477	100.00

**- Kinetics of enantiomerization of  $H_6(TMS)_2$  in 1,2-dimethoxybenzene**

About 0.4 mg of the second eluted enantiomer of  $H_6(TMS)_2$  is heated in about 25 mL of 1,2-dimethoxybenzene at 207 °C. 20  $\mu$ L are taken and then injected on (S,S)-Whelk-O1 (90:10 heptane / dichloromethane, 1 mL/min, UV 300 nm). The percentage decrease of the second eluted enantiomer of  $H_6(TMS)_2$  is monitored.

Time (min)	% second eluted enantiomer	$\ln ((\%t-50\%)/(\%t=0)-50\%))$
0	99.587	0.00000
1140	98.198	-0.02841
4040	94.601	-0.10597
5415	92.951	-0.14367
6915	91.329	-0.18216



$$k_{\text{enantiomerisation}} = 2.2091\text{E-}07 \text{ s}^{-1} \text{ (207}^\circ\text{C, 1,2-dimethoxybenzene)}$$

$$\Delta G^\ddagger = 180.7 \text{ kJ/mol (207}^\circ\text{C, 1,2-dimethoxybenzene)}$$

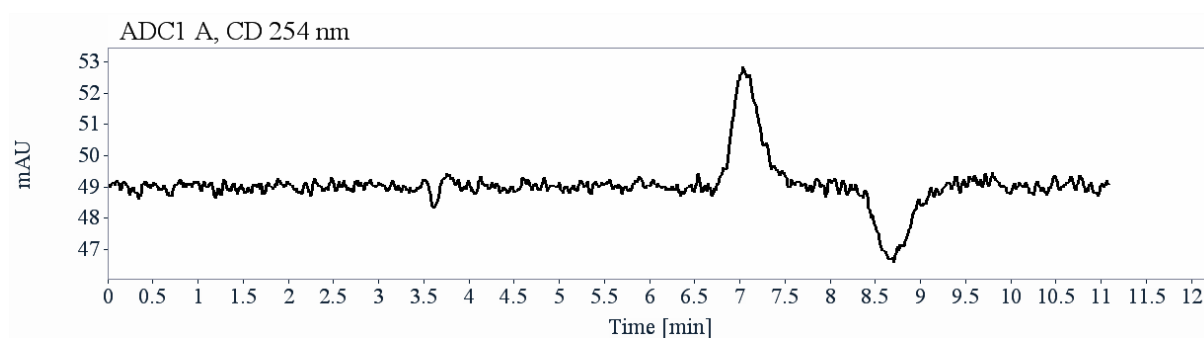
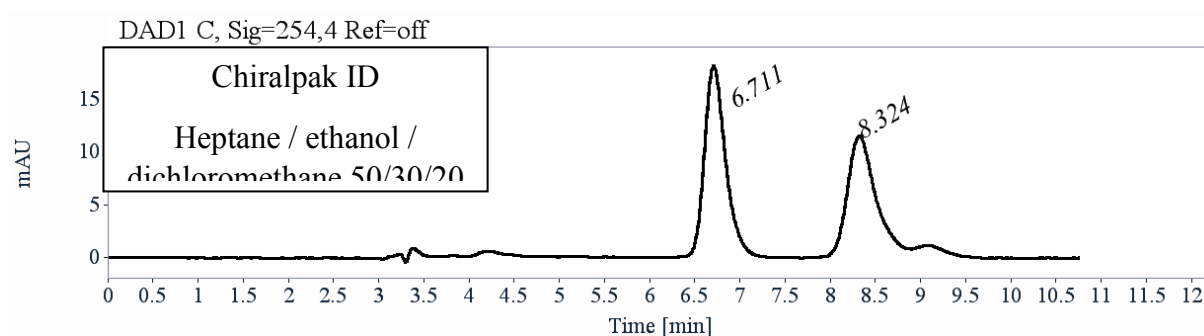
$$t_{1/2} = 18 \text{ days (207}^\circ\text{C, 1,2-dimethoxybenzene)}$$



**- Analytical chiral HPLC separation for  $H_6(DPP)_2$**

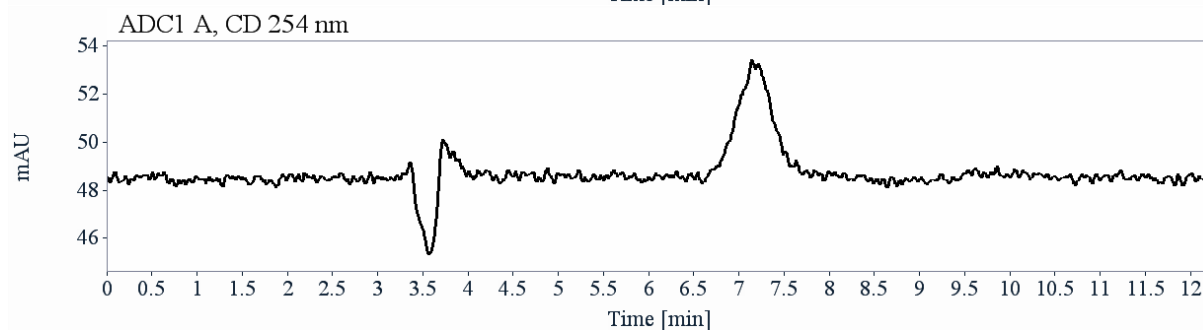
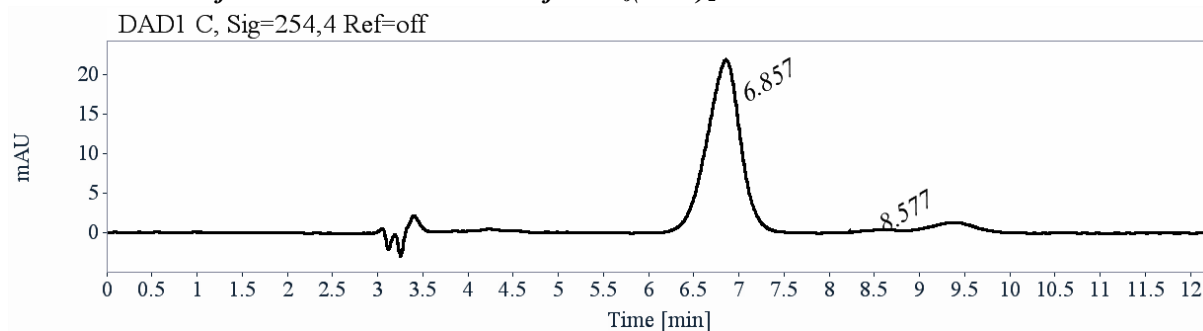
• A mixture of  $M$ - $H_6(DPP)_2$  and  $P$ - $(H_6(DPP)_2)$  is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and with circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	$\alpha$	Rs
Chiralpak ID	Heptane / ethanol / dichloromethane 50/30/20	6.71 (M)	1.27	8.32 (P)	1.82	1.43	3.38



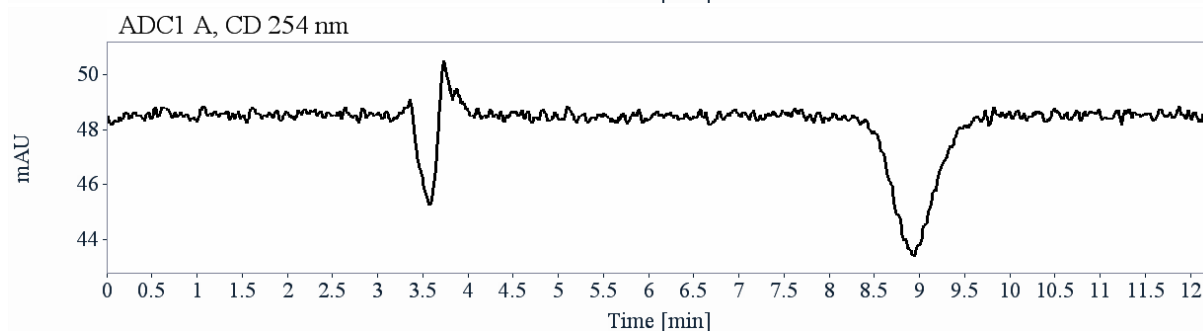
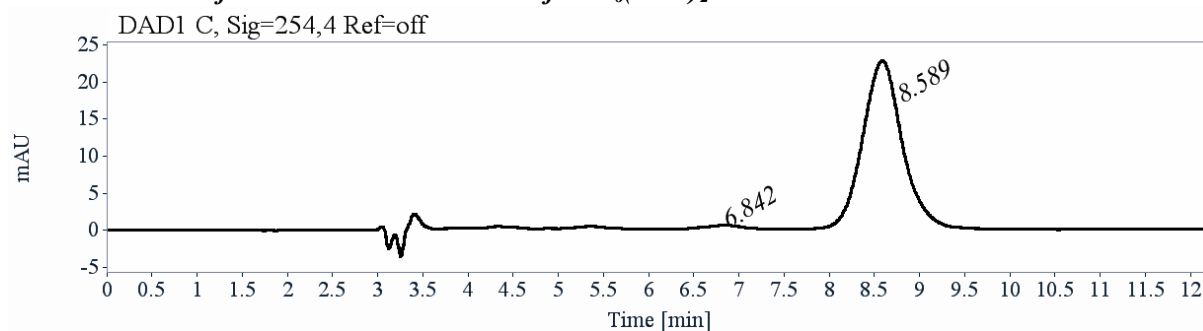
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.71	298	56.16	1.27		
8.32	233	43.84	1.82	1.43	3.38
Sum	531	100.00			

**- Determination of the enantiomeric excess of *M*-H<sub>6</sub>(DPP)<sub>2</sub>**



RT [min]	Area	Area%	Capacity Factor
6.86	570	97.54	1.32
8.58	14	2.46	1.91
Sum	585	100.00	

**- Determination of the enantiomeric excess of *P*-H<sub>6</sub>(DPP)<sub>2</sub>**

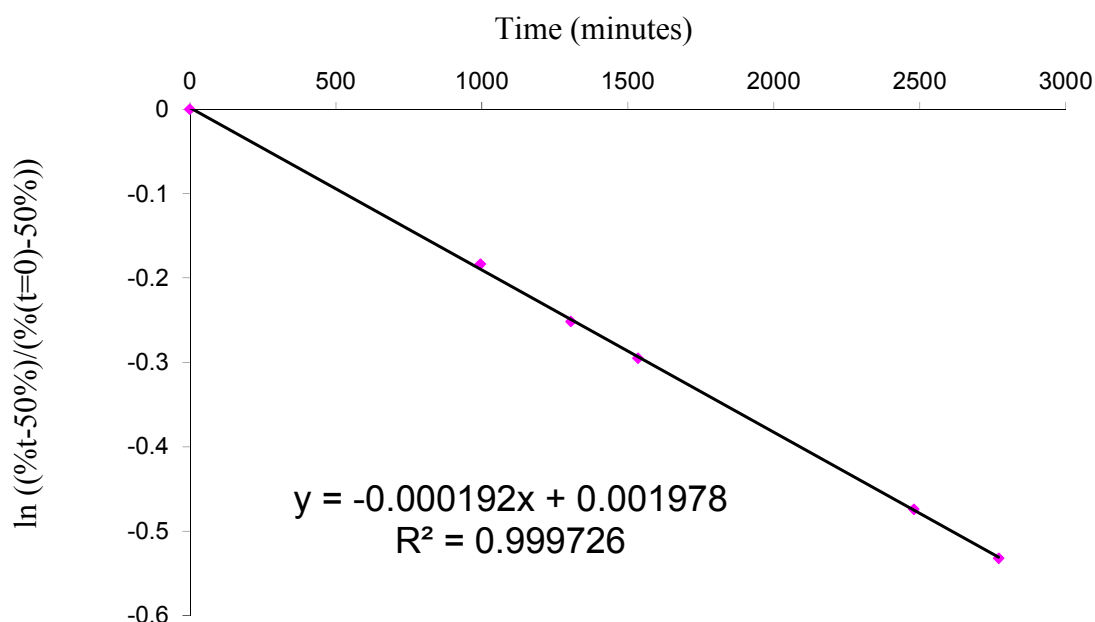


RT [min]	Area	Area%	Capacity Factor
6.84	16	2.20	1.32
8.59	705	97.80	1.91
Sum	721	100.00	

### - Kinetics of enantiomerization of $H_6(DPP)_2$ in 1,2-dichloro-benzene

About 0.3 mg of  $P-H_6(DPP)_2$  is heated in about 25 mL of 1,2-dichlorobenzene at 182 °C. 20  $\mu$ L are taken and then injected on (Chiralpak ID (50:30:20 heptane / ethanol / dichloromethane, 1 mL/min, UV 290 nm). The percentage decrease of  $P-H_6(DPP)_2$  is monitored.

Time (min)	% second eluted enantiomer	$\ln ((\%t-50\%)/(\%(t=0)-50\%))$
0	97.61	0.00000
995	89.63	-0.18346
1305	87.02	-0.25158
1535	85.44	-0.29520
2480	79.63	-0.47426
2770	77.96	-0.53227



$$k_{\text{enantiomerisation}} = 1.6040E-06 \text{ s}^{-1} \text{ (182}^\circ\text{C, 1,2-dichlorobenzene)}$$

$$\Delta G^\ddagger = 163.6 \text{ kJ/mol (182}^\circ\text{C, 1,2-dichlorobenzene)}$$

$$t_{1/2} = 60 \text{ hours (182}^\circ\text{C, 1,2-dichlorobenzene)}$$

### References

- <sup>1.1</sup> C. Würth, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nat. Protocols*, 2013, **8**, 1535.
- <sup>1.2</sup> E. Anger, M. Srebro, N. Vanthuyne, L. Toupet, S. Rigaut, C. Roussel, C.; J. Autschbach, J. Crassous, R. Réau, *J. Am. Chem. Soc.* 2012, **134**, 15628.
- <sup>1.3</sup> M. Jung, Y. Yoon, J. H. Park, W. Cha, A. Kim, J. Kang, S. Gautam, D. Seo, J. H. Cho, H. Kim, J. Y. Choi, K. H. Chae, K. Kwak, H. J. Son, M. J.; Ko, H. Kim, D.-K.; Lee, J. Y. Kim, D. H.; Choi, B. Kim, *ACS Nano*, 2014, **8**, 5988.

<sup>1.4</sup> M. Grzybowski, D. T. Gryko, *Adv. Opt. Mater.*, 2015, **3**, 280.

<sup>1.5</sup> (a) C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv. Mater.*, **2011**, **23**, 2367, (b) A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2001.

## 2. Computational part

### Computational details

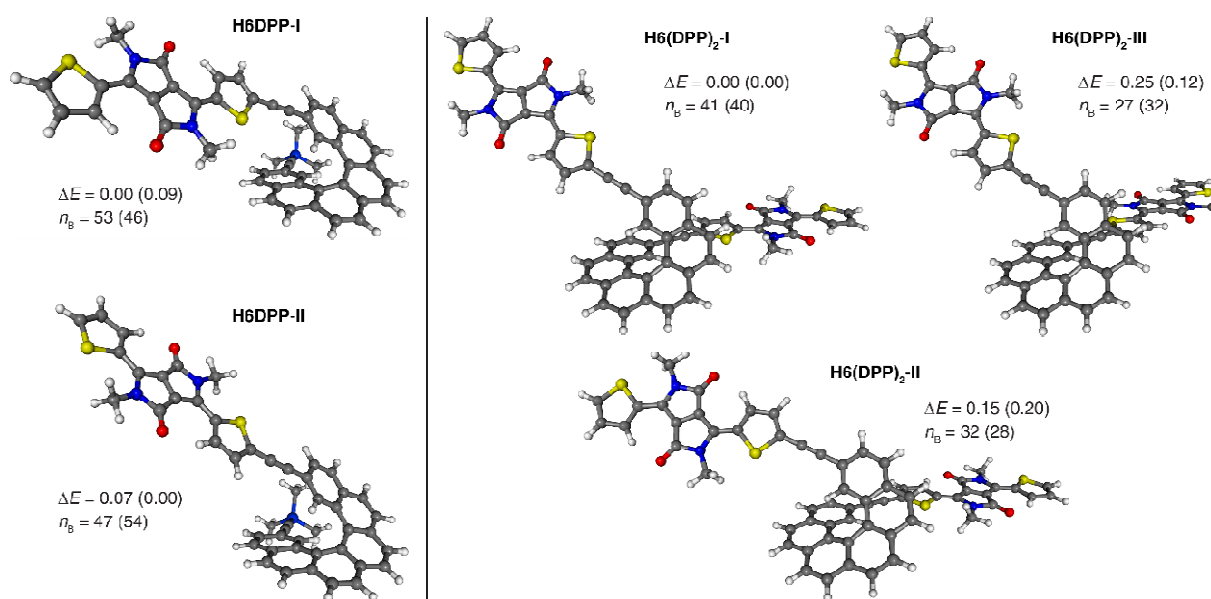
Computations were performed for **DPPBr** and **H6(TMS)<sub>2</sub>** reference systems and truncated models of helicene-DPP derivatives **H6DPP** and **H6(DPP)<sub>2</sub>** with *n*-octyl groups replaced by methyls.

All calculations were carried out with the Turbomole package (TM6.6),<sup>2.1</sup> and, where specifically stated, with the Gaussian 09 program (G09),<sup>2.2</sup> using Kohn-Sham (KS) density functional theory (KST, or DFT) and its time-dependent variant (TDKS, or TDDFT).<sup>2.3</sup> Geometry optimizations were performed using the BP<sup>2.4</sup> exchange-correlation functional and a split-valence basis set with one set of polarization functions for non-hydrogen atoms, SV(P).<sup>2.5</sup> TDDFT linear response calculations of singlet excitation energies as well as the associated dipole and rotatory strengths were carried out with BHLYP<sup>2.6</sup>/SV(P). Solvent effects (dichloromethane, DCM,  $\epsilon = 8.9$ ) were included in the calculations via the conductor-like screening model (COSMO) with the default parameters of the TM6.6/COSMO implementation.<sup>2.7</sup>

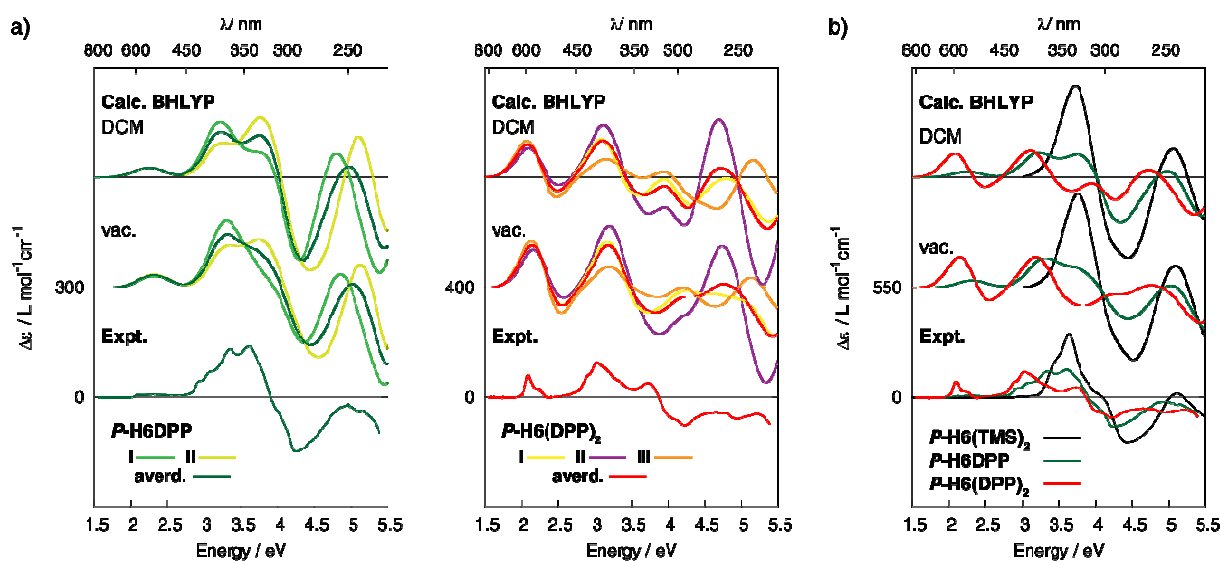
The TDDFT calculations reported here cover up to 150 lowest singlet excited states to assure that all transitions with a significant rotatory strength in the experimentally observed energy range are included. The simulated absorption and electronic circular dichroism (ECD) spectra shown are the sums of Gaussian functions centered at the vertical excitation energies and scaled using the calculated dipole and rotatory strengths, with a parameter of  $\sigma = 0.2$  eV applied for the root mean square width.<sup>2.8</sup>

Additional ECD calculations were performed on a (DPPBr)<sub>2</sub> dimer model, with the two DPP moieties in the same relative positions as adopted by the substituents in **H6(DPP)<sub>2</sub>** as well as (DPP-alkynyl)<sub>2</sub> and (DPP-alkynyl-Ph)<sub>2</sub> dimer models including the alkynyl group and the alkynyl with the first phenyl group of the helicene, respectively (see Figure S2.12). The dangling bonds were saturated with bromine or hydrogen atoms whose positions were optimized with BP/SV(P). The ECD computations utilized BHLYP and a functional based on PBE0<sup>2.9</sup> with range-separated exchange and correct asymptotic behavior (long-range correction = LC).<sup>2.10</sup> The LC-PBE0 parametrization afforded 25% of exact exchange in the short-range limit and employed an error-function range-separation with a separation parameter  $\gamma$  of  $0.30 \text{ a}_0^{-1}$ . These calculations were performed with G09. The polarizable continuum model (PCM)<sup>2.11</sup> was used here to simulate the solvent (DCM) effects.

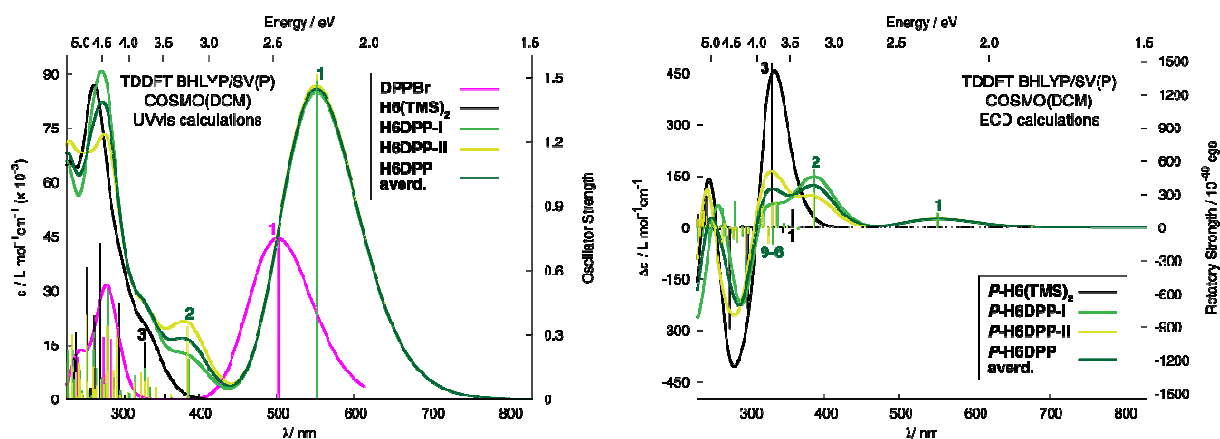
## Additional computational results



**Figure S2.1.** Selected low-energy structures of helicene-DPP derivatives **H6DPP** (left) and **H6(DPP)<sub>2</sub>** (right).  $\Delta E$  and  $n_B$  values are, respectively, relative energies (in kcal/mol) and the corresponding Boltzmann populations (in %) for geometries optimized using BP/SV(P) with continuum solvent model for  $\text{CH}_2\text{Cl}_2$  (displayed); in parentheses are given  $\Delta E$  for BP/SV(P) geometries optimized without the solvent model.



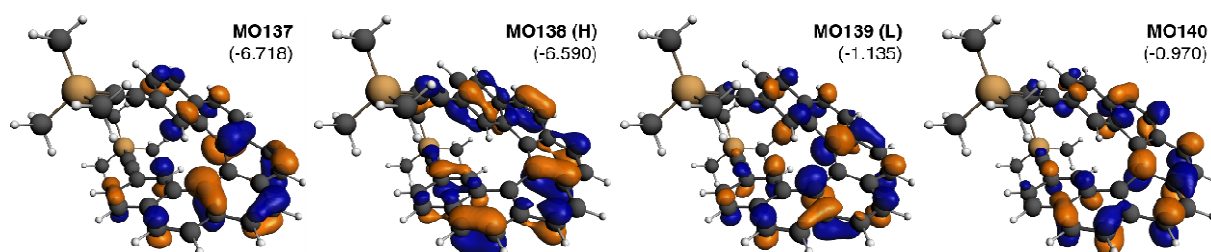
**Figure S2.2.** Comparison of the experimental and calculated TDDFT ECD spectra of helicene-DPP derivatives with helicene-TMS system used as a reference. No spectral shift has been applied. ‘vac.’ / ‘DCM’ indicates calculations without / with continuum solvent model (dichloromethane,  $\epsilon = 8.9$ ). Panel a: Numbers listed (I, II, III) correspond to different **H6DPP** and **H6(DPP)<sub>2</sub>** conformers (see Figure S2.1). ‘averd.’ indicates a Boltzmann-averaged (25°C) spectrum. Panel b: simulated spectra correspond to Boltzmann-averaged (25°C) spectra from panel a.



**Figure S2.3.** Comparison of the simulated UVvis (left) and ECD (right) spectra of **H6DPP** with **H6(TMS)<sub>2</sub>** and **DPPBr** used as a reference. No spectral shift has been applied. Calculated excitation energies and rotatory strengths indicated as ‘stick’ spectra. Numbered excitations correspond to those analyzed in detail. ‘avard.’ indicates a Boltzmann-averaged (25°C) spectrum.

**Table S2.1.** Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the *P*-**H6(TMS)<sub>2</sub>**.

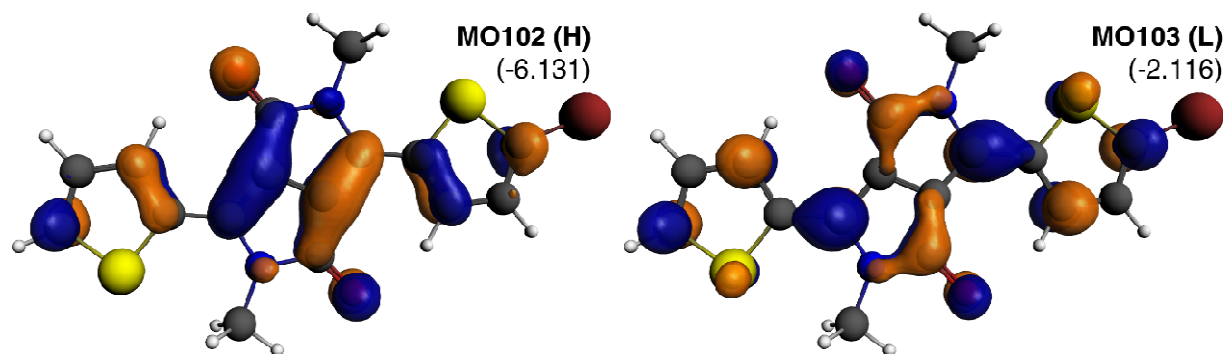
Excitation	$E / \text{eV}$	$\lambda / \text{nm}$	$f$	$R / 10^{-40}$ cgs	occ no.	unocc no.	%
1	3.47	357	0.025	159.37	138	139	64.7
					137	140	20.5
3	3.75	330	0.267	1477.02	137	140	62.5
					138	139	24.1



**Figure S2.4.** Isosurfaces ( $\pm 0.04$  au) of MOs involved in selected transitions of *P*-**H6(TMS)<sub>2</sub>**. ‘H’ = HOMO, ‘L’ = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.

**Table S2.2.** Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the **DPPBr**.

Excitation	$E / \text{eV}$	$\lambda / \text{nm}$	$f$	occ no.	unocc no.	%
1	2.47	502	0.779	102	103	98.3



**Figure S2.5.** Isosurfaces ( $\pm 0.04$  au) of MOs involved in selected transitions of **DPPBr**. ‘H’ = HOMO, ‘L’ = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.

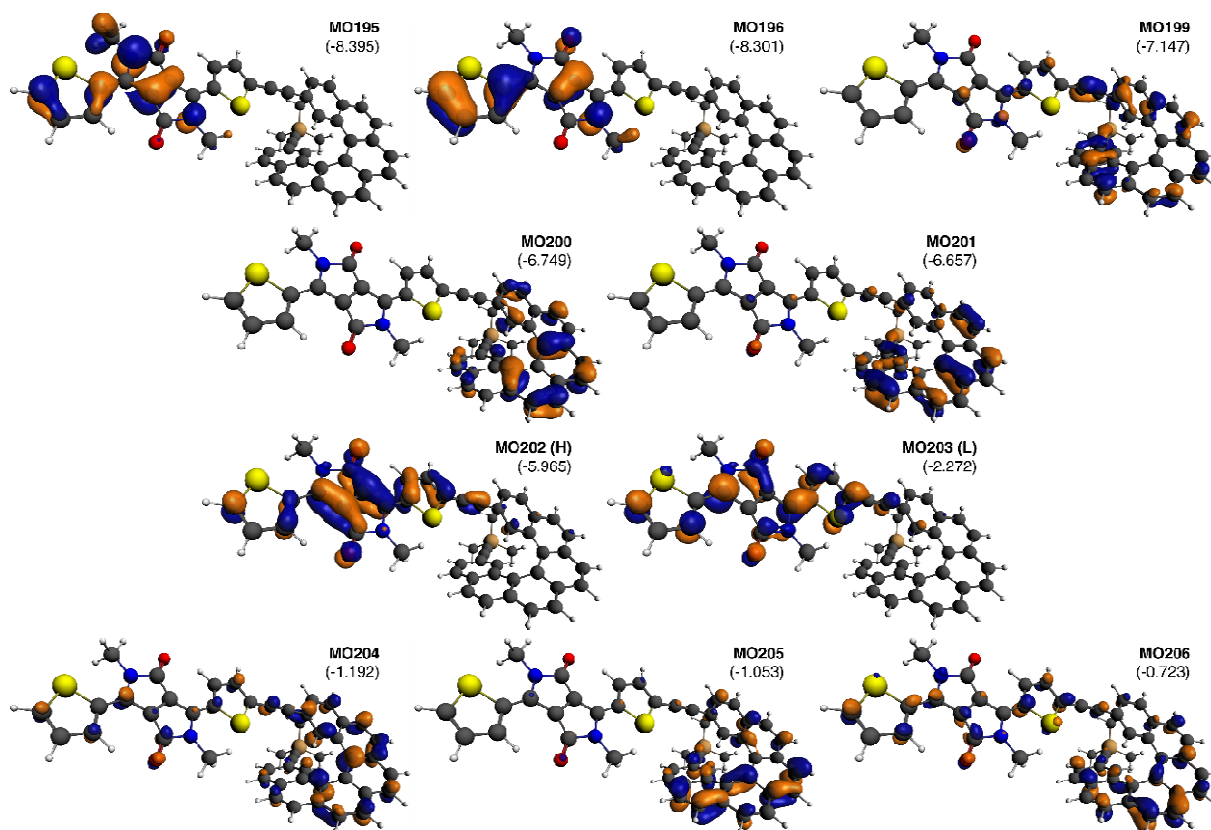
**Table S2.3.** Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the **P-H6DPP-I**.

Excitation	$E / \text{eV}$	$\lambda / \text{nm}$	$f$	$R / 10^{-40}$ cgs	occ no.	unocc no.	%
1	2.25	552	1.483	130.73	202	203	95.4
					201	204	0.86
					199	204	0.52
2	3.20	387	0.189	532.45	201	203	42.1
					202	204	13.1
					199	203	12.7
6	3.67	337	0.060	201.48	201	205	26.2
					200	203	23.7
					201	203	14.1
					202	205	10.1
7	3.75	331	0.147	-145.71	199	203	30.0
					195	203	15.9
					200	205	13.3
8	3.81	326	0.084	-83.82	195	203	32.1
					196	203	22.7
					199	203	18.5
9	3.91	317	0.113	223.36	200	206	19.6
					202	206	14.0
					200	204	10.6

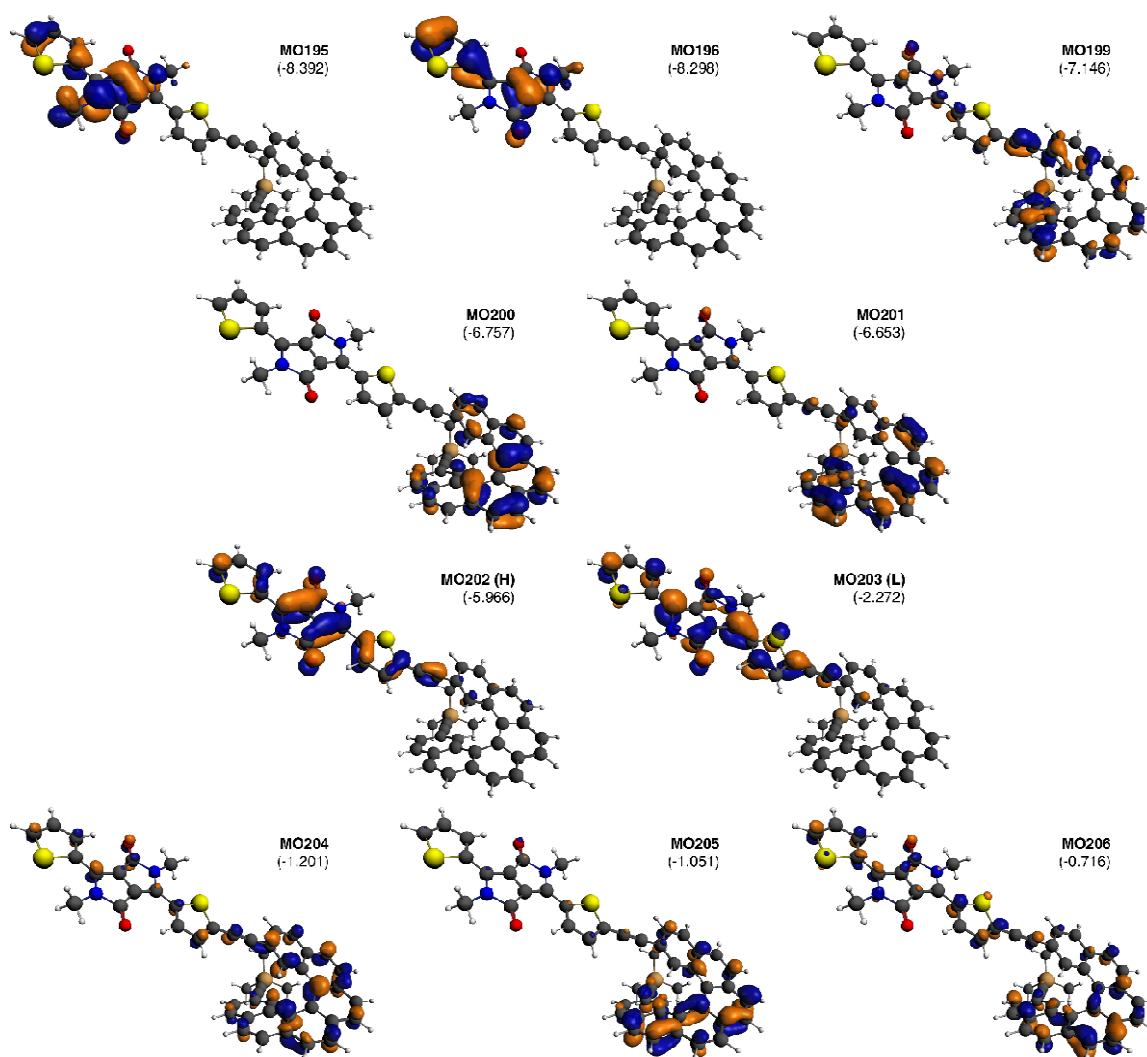
**Table S2.4.** Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the *P-H6DPP-II*.

Excitation	$E / \text{eV}$	$\lambda / \text{nm}$	$f$	$R / 10^{-40} \text{ cgs}$	occ no.	unocc no.	%
1	2.25	552	1.513	136.64	202	203	95.3
					201	204	0.91
					199	204	0.54
2	3.21	386	0.340	321.99	201	203	42.2
					202	204	13.5
					199	203	13.3
6	3.70	335	0.102	237.57	201	205	27.9
					200	203	27.8
					201	203	11.8
7	3.75	330	0.082	201.30	199	203	25.2
					195	203	20.8
					196	203	12.5
					200	205	12.0
8	3.81	326	0.122	-133.34	195	203	27.3
					199	203	23.0
					196	203	20.4
9	3.92	316	0.079	217.45	200	206	20.6
					202	206	12.9

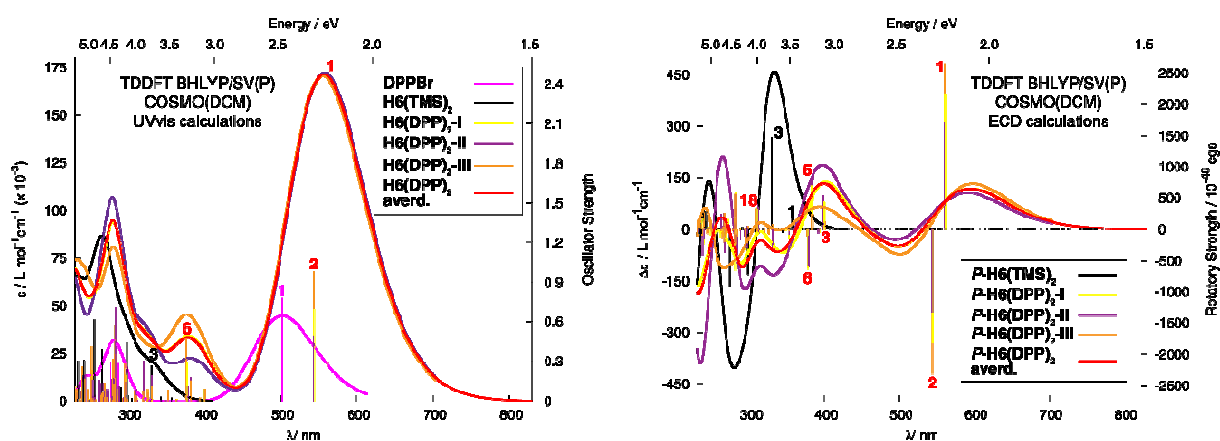




**Figure S2.6.** Isosurfaces ( $\pm 0.04$  au) of MOs involved in selected transitions of *P*-H6DPP-I. ‘H’ = HOMO, ‘L’ = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.



**Figure S2.7.** Isosurfaces ( $\pm 0.04$  au) of MOs involved in selected transitions of *P*-H6DPP-II. ‘H’ = HOMO, ‘L’ = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.



**Figure S2.8.** Comparison of the simulated UVvis (left) and ECD (right) spectra of **H6(DPP)<sub>2</sub>** with **H6(TMS)<sub>2</sub>** and **DPPBr** used as a reference. No spectral shift has been applied. Calculated excitation energies and rotatory strengths indicated as ‘stick’ spectra. Numbered excitations correspond to those analyzed in detail. ‘averd.’ indicates a Boltzmann-averaged (25°C) spectrum.

**Table S2.5.** Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the *P-H6(DPP)<sub>2</sub>-I*. See also Table S2.8.

Excitation	$E / \text{eV}$	$\lambda / \text{nm}$	$f$	$R / 10^{-40} \text{ cgs}$	occ no.	unocc no.	%
1	2.21	561	2.316	2180.80	266	267	51.0
					265	268	43.9
2	2.28	544	0.695	-1820.38	265	267	47.7
					266	268	47.6
3	3.10	400	0.089	438.52	265	268	28.2
					264	267	24.5
					266	267	23.3
5	3.24	382	0.169	702.33	265	268	19.4
					266	267	19.3
					264	267	17.5
					262	268	11.5
6	3.29	377	0.298	-641.88	264	268	29.0
					262	267	15.2
					263	267	13.5
18	4.00	310	0.080	350.90	263	270	20.3
					263	268	15.9
					265	272	13.3
					263	272	11.7

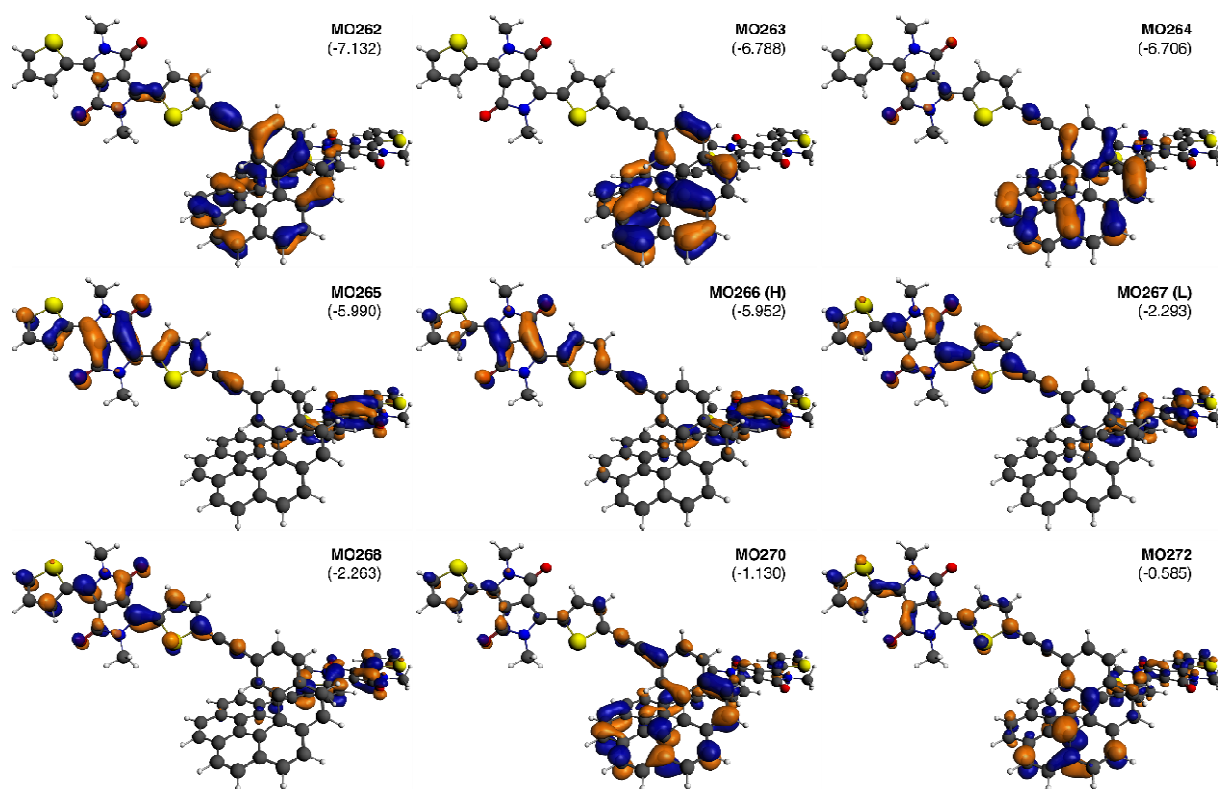
**Table S2.6.** Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the *P-H6(DPP)<sub>2</sub>-II*. See also Table S2.9.

Excitation	$E / \text{eV}$	$\lambda / \text{nm}$	$f$	$R / 10^{-40} \text{ cgs}$	occ no.	unocc no.	%
1	2.21	561	2.531	1708.48	266	267	50.7
					265	268	44.4
2	2.28	543	0.493	-1331.97	266	268	47.7
					265	267	47.7
3	3.11	398	0.091	541.66	265	268	27.2
					264	267	26.0
					266	267	22.4
5	3.24	382	0.178	794.14	265	268	19.1
					266	267	19.1
					264	267	15.3
					263	268	11.8

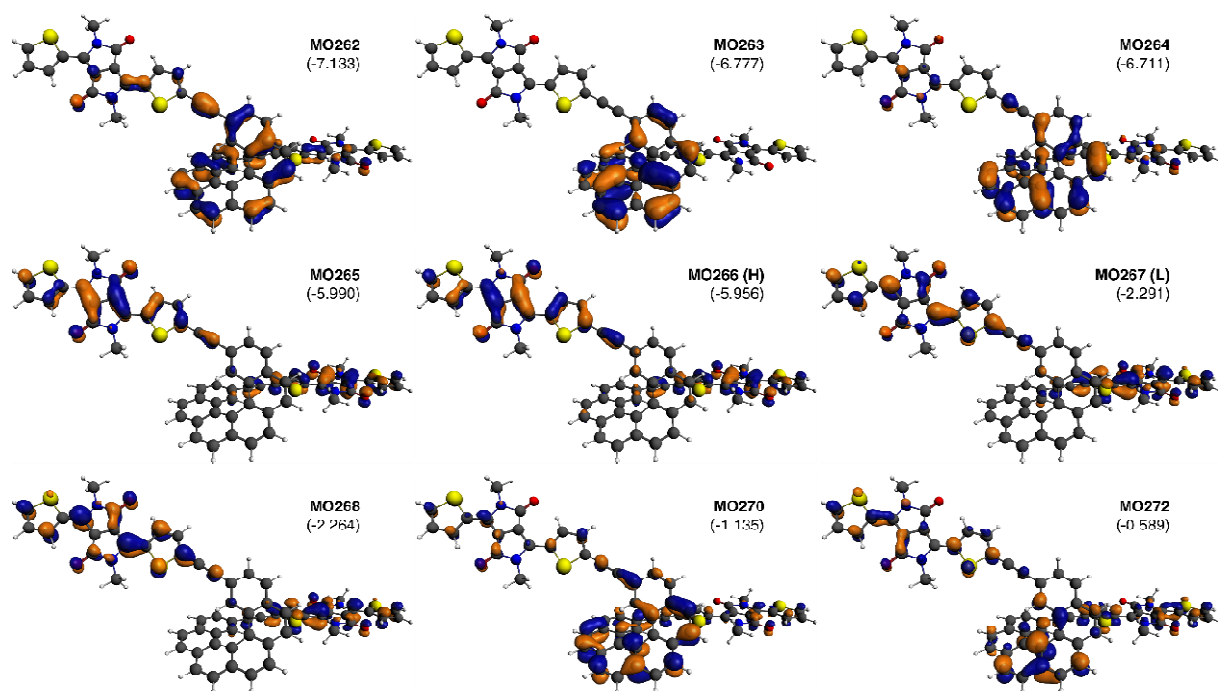
					262	268	11.0
6	3.28	378	0.111	-596.00	264	268	26.9
					263	267	15.4
					262	267	14.8
18	3.99	311	0.087	406.16	263	270	21.0
					265	272	14.5
					263	268	13.7
					263	272	11.2

**Table S2.7.** Selected dominant excitations and occupied (occ) – unoccupied (unocc) MO pair contributions (greater than 10%) of the *P*-**H6(DPP)<sub>2</sub>-III**. See also Table S2.10.

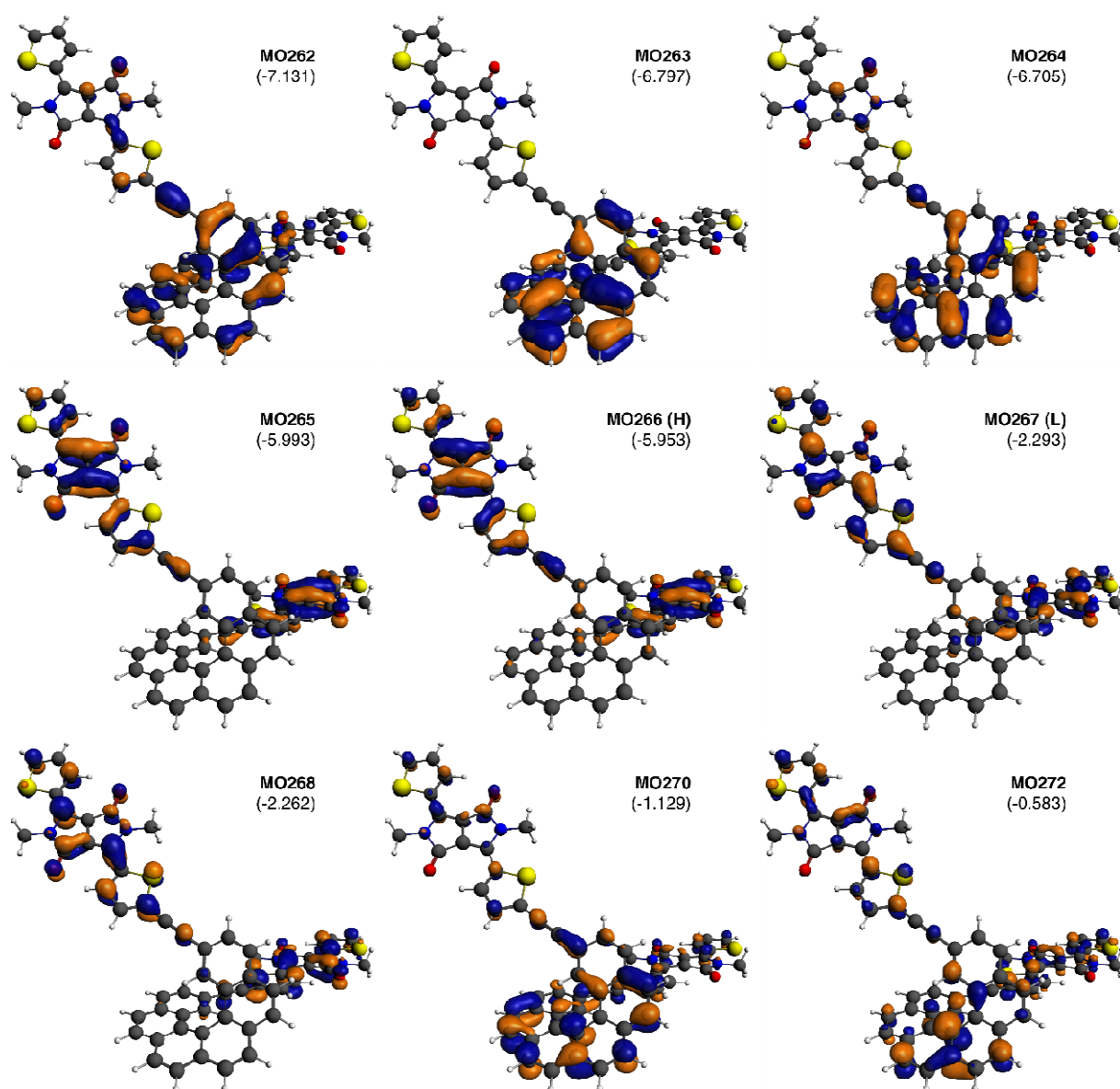
Excitation	<i>E</i> / eV	$\lambda$ / nm	<i>f</i>	<i>R</i> / 10 <sup>-40</sup> cgs	occ no.	unocc no.	%
1	2.21	561	2.031	2657.21	266	267	51.4
					265	268	43.9
2	2.28	544	0.980	-2319.67	265	267	47.7
					266	268	47.6
3	3.10	401	0.090	122.34	265	268	30.1
					266	267	23.9
5	3.24	382	0.156	243.01	265	268	19.7
					266	267	19.5
					264	267	19.5
					262	268	11.9
6	3.30	376	0.489	-104.72	264	268	30.7
					262	267	15.8
					263	267	11.9
18	4.02	309	0.076	336.46	263	270	20.7
					263	268	19.0
					265	272	12.9
					263	272	12.7



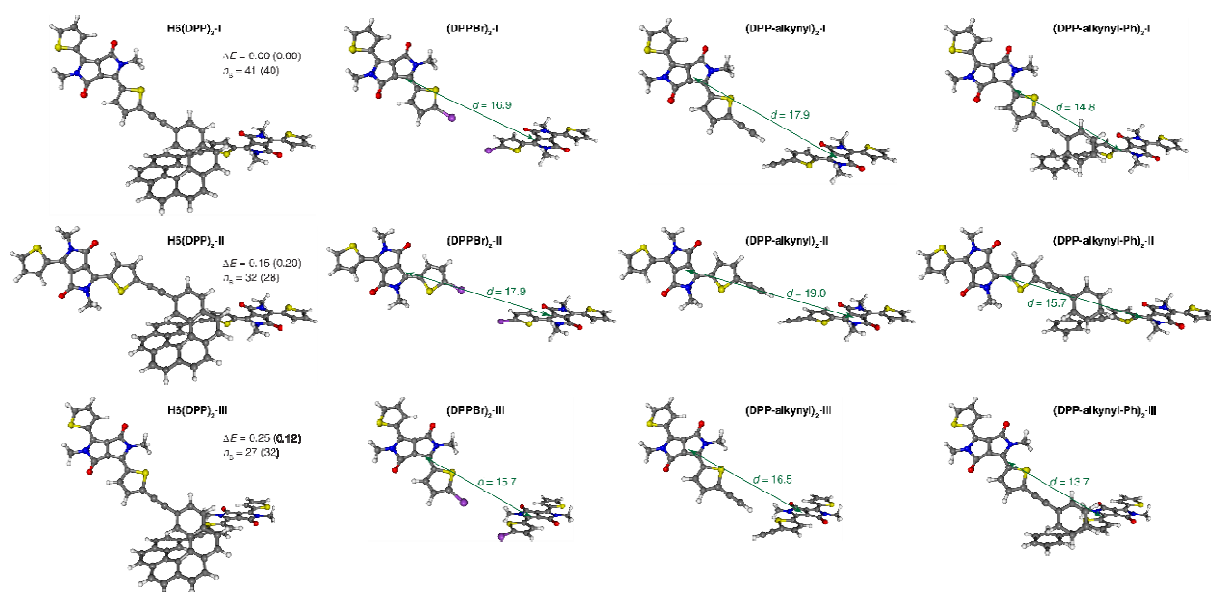
**Figure S2.9.** Isosurfaces ( $\pm 0.03$  au) of MOs involved in selected transitions of  $P\text{-H6(DPP)}_2\text{-I}$ . 'H' = HOMO, 'L' = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.



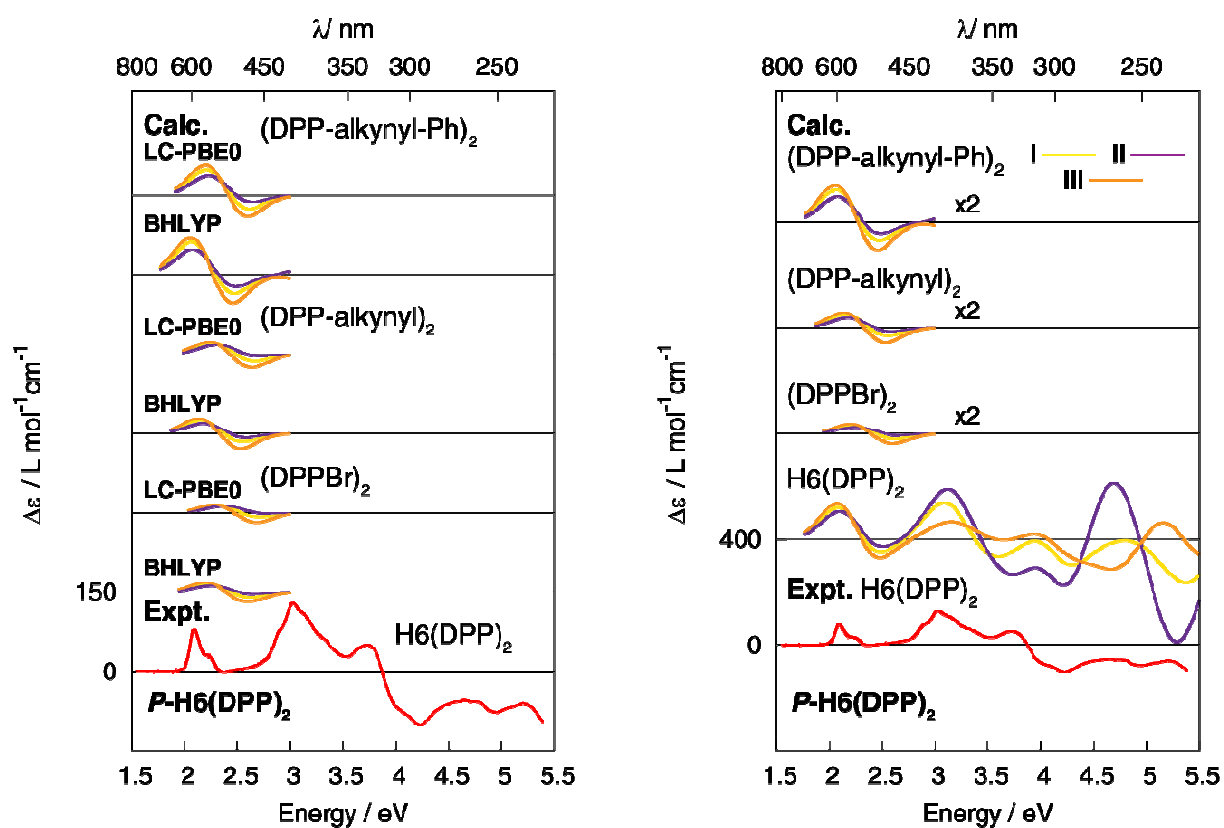
**Figure S2.10.** Isosurfaces ( $\pm 0.03$  au) of MOs involved in selected transitions of  $P\text{-H6(DPP)}_2\text{-II}$ . 'H' = HOMO, 'L' = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.



**Figure S2.11.** Isosurfaces ( $\pm 0.03$  au) of MOs involved in selected transitions of *P*-H6(DPP)<sub>2</sub>-III. ‘H’ = HOMO, ‘L’ = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV.



**Figure S2.12.** Selected low-energy structures of **H6(DPP)<sub>2</sub>** derivatives and the corresponding **(DPPBr)<sub>2</sub>**, **(DPP-alkynyl)<sub>2</sub>** and **(DPP-alkynyl-Ph)<sub>2</sub>** dimer models.  $\Delta E$  and  $n_B$  values listed for **H6(DPP)<sub>2</sub>** complexes are, respectively, relative energies (in kcal/mol) and the corresponding Boltzmann populations (in %) for geometries optimized using BP/SV(P) with continuum solvent model for CH<sub>2</sub>Cl<sub>2</sub> (displayed); in parentheses are given  $\Delta E$  for BP/SV(P) geometries optimized without the solvent model. For dimer models, a distance between centers of nuclear charge of both chromophores ( $d$ , in Å) is given.



**Figure S2.13.** Right: Comparison of the experimental ECD spectrum of **H6(DPP)<sub>2</sub>** and calculated (TDDFT with continuum solvent model for dichloromethane) ECD spectra (limited to low-energy

region, < 3 eV) of the corresponding dimer models (see Figure S2.12). Left: Comparison of the experimental and simulated (TDDFT BHLYP) ECD spectra of **H6(DPP)<sub>2</sub>** derivatives and the corresponding dimer models. Intensity of the simulated ECD spectra of dimer systems has been scaled by a factor of 2 for visual clarity. Numbers listed (I, II, III) correspond to different conformers examined. No spectral shift has been applied.

**Table S2.8.** Lowest-energy excitations and occupied (occ) – unoccupied (unocc) MO pair contributions of the *P*-**H6(DPP)<sub>2</sub>-I** and the corresponding **(DPPBr)<sub>2</sub>-I** and **(DPP-alkynyl-Ph)<sub>2</sub>-I**. BHLYP DCM calculations. See Figure S2.14.

Excitation	<i>E</i> / eV	$\lambda$ / nm	<i>f</i>	<i>R</i> / 10 <sup>-40</sup> cgs	occ no.	unocc no.	%
<b>H6(DPP)<sub>2</sub>-I</b>							
1	2.21	561	2.316	2180.80	266	267	51.0
					265	268	43.9
					264	269	1.28
					262	270	0.64
2	2.28	544	0.695	-1820.38	265	267	47.7
					266	268	47.6
					264	270	0.90
					262	269	0.62
					264	268	0.61
<b>(DPPBr)<sub>2</sub>-I</b>							
1	2.39	519	1.378	990.61	203	205	48.9
					204	206	50.3
2	2.41	514	0.325	-962.01	203	205	50.3
					204	206	48.9
<b>(DPP-alkynyl-Ph)<sub>2</sub>-I</b>							
1	2.21	560	2.275	1580.52	222	223	50.7
					221	224	46.0
2	2.27	547	0.507	-1429.97	221	223	49.1
					222	224	47.6

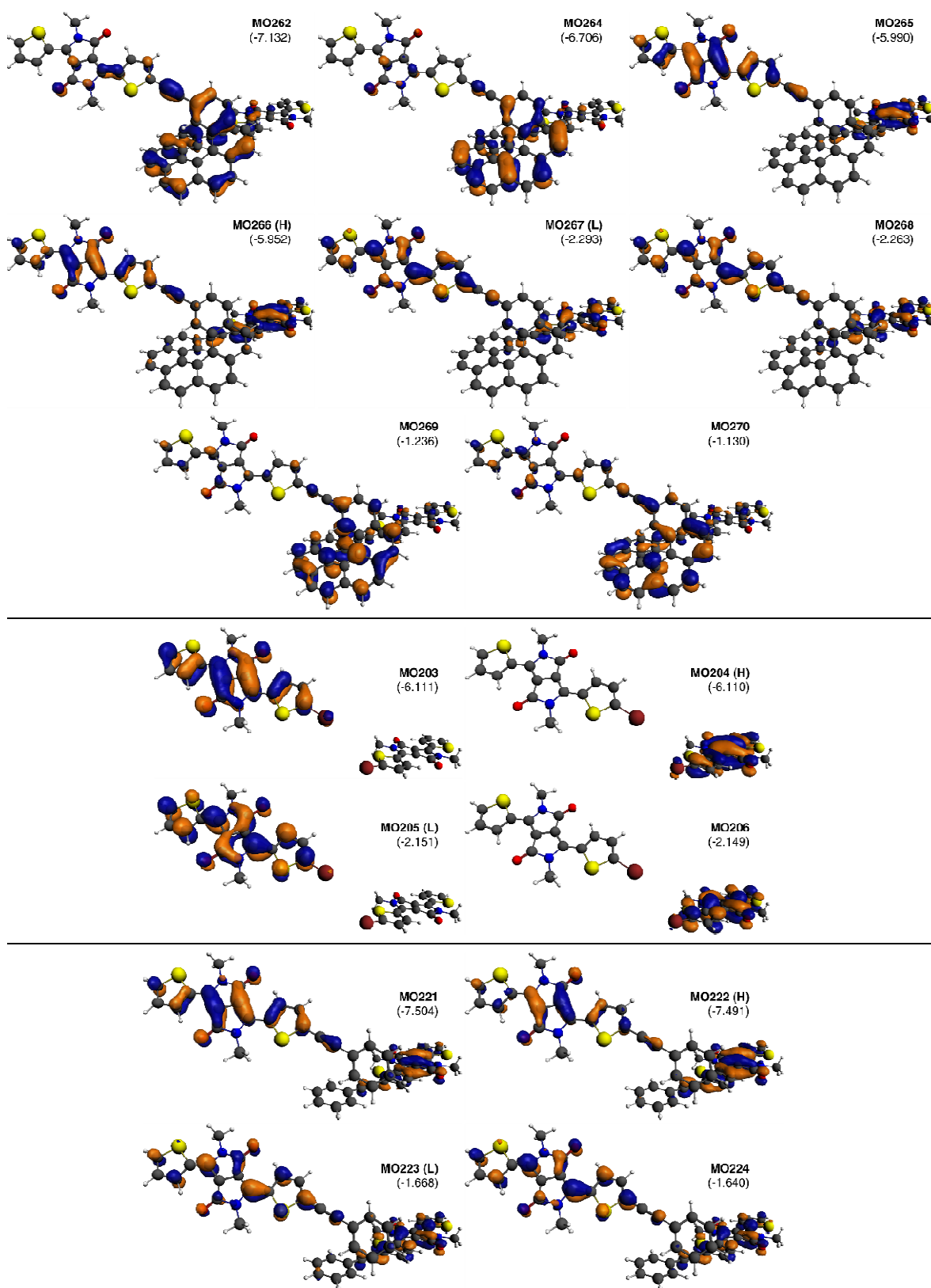


**Table S2.9.** Lowest-energy excitations and occupied (occ) – unoccupied (unocc) MO pair contributions of the *P*-**H6(DPP)<sub>2</sub>-II** and the corresponding **(DPPBr)<sub>2</sub>-II** and **(DPP-alkynyl-Ph)<sub>2</sub>-II**. BHLYP DCM calculations. See Figure S2.14.

Excitation	<i>E</i> / eV	$\lambda$ / nm	<i>f</i>	<i>R</i> / 10 <sup>-40</sup> cgs	occ no.	unocc no.	%
<b>H6(DPP)<sub>2</sub>-II</b>							
1	2.21	561	2.531	1708.48	266	267	50.7
					265	268	44.4
					264	269	1.22
					262	270	0.63
2	2.28	543	0.493	-1331.97	266	268	47.7
					265	267	47.7
					264	270	0.89
					262	269	0.59
					264	268	0.57
<b>(DPPBr)<sub>2</sub>-II</b>							
1	2.39	518	1.453	607.89	203	205	49.4
					204	206	49.7
2	2.41	514	0.257	-571.33	203	205	49.8
					204	206	49.4
<b>(DPP-alkynyl-Ph)<sub>2</sub>-II</b>							
1	2.21	560	2.467	1116.38	222	223	50.5
					221	224	46.2
2	2.27	546	0.347	-976.42	221	223	49.3
					222	224	48.4

**Table S2.10.** Lowest-energy excitations and occupied (occ) – unoccupied (unocc) MO pair contributions of the *P*-**H6(DPP)<sub>2</sub>-III** and the corresponding **(DPPBr)<sub>2</sub>-III** and **(DPP-alkynyl-Ph)<sub>2</sub>-III**. BHLYP DCM calculations. See Figure S2.14.

Excitation	<i>E</i> / eV	$\lambda$ / nm	<i>f</i>	<i>R</i> / 10 <sup>-40</sup> cgs	occ no.	unocc no.	%
<b>H6(DPP)<sub>2</sub>-III</b>							
1	2.21	561	2.031	2657.21	266	267	51.4
					265	268	43.9
					264	269	1.33
					262	270	0.66
2	2.28	544	0.980	-2319.67	265	267	47.7
					266	268	47.6
					264	270	0.90
					262	269	0.64
264	268	0.64					
<b>(DPPBr)<sub>2</sub>-III</b>							
1	2.39	518	1.250	1397.52	203	205	47.5
					204	206	50.8
2	2.41	514	0.446	-1391.14	203	205	51.1
					204	206	47.8
<b>(DPP-alkynyl-Ph)<sub>2</sub>-III</b>							
1	2.22	559	1.999	2038.28	222	223	50.8
					221	224	46.5
2	2.27	546	0.743	-1920.42	221	223	49.3
					222	224	48.3



**Figure S2.14.** Isosurfaces ( $\pm 0.03$  au) of MOs involved in transitions of lowest-energy excitations of **H6(DPP)<sub>2</sub>-I** (top), **(DPPBr)<sub>2</sub>-I** (middle) and **(DPP-alkynyl-Ph)<sub>2</sub>-I** (bottom). ‘H’ = HOMO, ‘L’ = LUMO. Values listed in the parentheses are the corresponding orbital energies, in eV. Isosurfaces of the corresponding MOs for conformers II and III appeared to be very similar and therefore they are not shown.

## Analysis of exciton coupling effect in **H6(DPP)<sub>2</sub>**

In order to confirm the presence of an exciton coupling mechanism in **H6(DPP)<sub>2</sub>**, calculations were performed on a (DPPBr)<sub>2</sub> dimer in the same arrangement as the substituents in **H6(DPP)<sub>2</sub>**, as well as a (DPP-alkynyl-H)<sub>2</sub> dimer including the alkynyl group and a (DPP-alkynyl-Ph)<sub>2</sub> model including the alkynyl and the first phenyl group of the helicene (Figure S2.12). The corresponding calculated ECD spectra of the dimer models indeed show very similar spectral shapes as **H6(DPP)<sub>2</sub>** below 450 nm (Figure S2.13). The (DPPBr)<sub>2</sub> model produces rotatory strengths that are a factor of 2 to 3 lower than those of the **H6(DPP)<sub>2</sub>** rotamers, but they are already much larger than the rotatory strengths of the DPP-centered transitions in the mono-substituted **H6DPP**. The energetic splitting of the two coupled excitations is only 0.02 eV, and therefore the broadened ECD intensity remains much weaker for this model than for **H6(DPP)<sub>2</sub>**. When the coupled chromophores are extended, in models (DPP-alkynyl-H)<sub>2</sub> and (DPP-alkynyl-Ph)<sub>2</sub>, the exciton couplets increase dramatically in intensity, which goes along with a delocalization of the DPP frontier orbitals through the alkynyl into the phenyl groups (Figure S2.14) and an energetic splitting of the coupled excitations (0.05 to 0.06 eV) that is almost as large as in **H6(DPP)<sub>2</sub>** (0.07 eV). The rotatory strengths calculated for the lowest-energy exciton couplet of the (DPP-alkynyl-Ph)<sub>2</sub> model come close to those of **H6(DPP)<sub>2</sub>**. However, the simulated ECD intensities remain lower for the models, showing that the full helicene bridge in **H6(DPP)<sub>2</sub>** enhances the intensity of the couplet even further. The dimer model spectra also show that the resulting exciton CD couplet may appear conservative or not, depending on the relative orientations of the DPP moieties to each other.

Figure S2.14 displays the MOs involved in the exciton couplet of two of the model dimers and **H6(DPP)<sub>2</sub>** (based on conformer I). The assignment of the two lowest energy excitations for all three conformers of the (DPPBr)<sub>2</sub> is an approximately 50-50 mix of HOMO-1-to-LUMO and HOMO-to-LUMO+1, respectively. The HOMO-1 and LUMO are centered on one of the DPPBr, while the HOMO and LUMO+1 are centered on the other DPPBr. Therefore, the calculation indeed produces the coupled pair of one-electron excitations expected for an exciton coupling between essentially non-interacting chromophores. The relevant (DPP-alkynyl-Ph)<sub>2</sub> model frontier orbitals appear as  $\pm$  linear combinations of the DPP orbitals, similar to those in the full **H6(DPP)<sub>2</sub>** system. The small energetic splitting between HOMO-1 and HOMO, and LUMO and LUMO+1, respectively, indicates weak through-space electrostatic interactions in the dimer model. The models for *P*-**H6(DPP)<sub>2</sub>** therefore show unambiguously that the longest-wavelength ECD band is caused by exciton coupling between the two electric transition dipoles of the DPP-alkynyl-phenyl fragments at the extremities of *P*-**H6(DPP)<sub>2</sub>**, with minor contributions of the central part of the helicene.

**Optimized (BP/SV(P) with the continuum solvent model for CH<sub>2</sub>Cl<sub>2</sub>) geometries of helicene-DPP derivatives along with the corresponding absolute energies:**

The atomic symbol followed by three Cartesian coordinates, in Å.

<b>DPPBr</b>		C	-1.8569420	0.4315637	-1.2095431		
Total energy = -4246.074553 au		C	-2.7475777	-0.6679603	-0.9933778		
C	0.8528512	1.3601255	0.8121911	C	-0.6255275	-3.5526838	-2.1196333
N	-0.2270727	1.3344677	1.6909209	C	0.5841667	-3.7742580	-2.7356029
C	-1.1691518	0.2959043	1.3447281	C	1.5438848	-2.7161426	-2.8965879
O	-2.2032035	0.0942854	1.9957992	C	1.3062474	-1.4236717	-2.3178765
C	-0.5888600	-0.3287203	0.1725028	C	2.7133096	-2.9507810	-3.6892457
C	0.6394423	0.3297736	-0.1324707	C	3.5713633	-1.9127957	-3.9777840
C	1.2170478	-0.2913207	-1.3082754	C	3.4271876	-0.6467001	-3.3245844
O	2.2527063	-0.0954495	-1.9579039	C	2.3983590	-0.4540288	-2.3311668
N	0.2688924	-1.3236735	-1.6598507	C	4.3114365	0.4269094	-3.6650059
C	0.5125286	-2.1771135	-2.8080460	C	4.2107236	1.6447386	-3.0295208
C	-0.8103027	-1.3483721	-0.7806670	C	3.3682093	1.7872117	-1.8802772
H	1.4792237	-1.8472855	-3.2423651	C	2.5513938	0.6918539	-1.4387123
H	-0.2815888	-2.0638728	-3.5782907	C	3.3933643	3.0208445	-1.1429468
H	0.6003327	-3.2455474	-2.5123553	C	2.7252516	3.1516408	0.0522886
C	-0.4739691	2.1888107	2.8381624	C	2.0824081	2.0151475	0.6441021
H	-0.5736727	3.2552219	2.5396023	C	2.0299584	0.7623837	-0.0713221
H	0.3276650	2.0882992	3.6020765	C	1.5482533	-0.3733254	0.6330932
H	-1.4340503	1.8486637	3.2789624	C	1.0613079	-0.2898535	1.9513451
C	1.9678213	2.2726586	0.8614602	C	1.0401056	0.9811032	2.6098103
C	3.0465389	2.2763968	-0.0385372	C	1.5525910	2.0955254	1.9653637
H	3.1105613	1.5502419	-0.8661940	C	0.5970438	-1.4598222	2.6295296
C	4.0023113	3.2890029	0.2345752	C	0.1859276	-2.4642592	3.2249848
H	4.9144574	3.4516548	-0.3593180	C	-2.3023323	1.7736503	-0.9987405
C	3.6655575	4.0619063	1.3377999	C	-2.6925820	2.9324673	-0.8055480
H	4.2142948	4.9085434	1.7746867	Si	-0.4344407	-3.9949973	4.0738599
S	2.1770968	3.5594642	2.0548406	H	0.6429895	1.0554603	3.6345015
C	-1.9386215	-2.2425341	-0.8425174	H	1.5832288	3.0675814	2.4853940
S	-2.1768745	-3.4873249	-2.0773723	H	2.7341392	4.1067949	0.6028653
C	-3.0140886	-2.2486918	0.0605280	H	3.9721218	3.8630594	-1.5577458
H	-3.0583580	-1.5441815	0.9087061	H	4.8341895	2.4996313	-3.3398587
C	-4.0037658	-3.2216230	-0.2282129	H	5.0479574	0.2679554	-4.4701418
H	-4.9172096	-3.3754578	0.3641952	H	4.4043689	-2.0475274	-4.6877317
C	-3.6867911	-3.9661696	-1.3573174	H	2.8650683	-3.9506486	-4.1285500
Br	-4.6917485	-5.3580829	-2.1220438	H	0.8399145	-4.7724557	-3.1285595
<b>H6(TMS)<sub>2</sub></b>				H	-1.3489243	-4.3737361	-1.9841443
Total energy = -1969.002266 au				H	-3.0170184	-2.8055613	-1.1429438
C	-2.3205112	-1.9586636	-1.2612118	H	-3.7740468	-0.4749273	-0.6436283
C	-0.9994828	-2.2258728	-1.7262472	H	0.1176682	1.0357394	-1.8210388
C	-0.0579447	-1.1403605	-1.8646296	H	1.5806823	-1.3622544	0.1569424
C	-0.5394430	0.1761346	-1.6346914	Si	-3.2181266	4.6884886	-0.5087101

C	-0.1842751	-3.7949245	5.9437855	C	2.5413199	-2.3534818	-0.0042489
C	-2.2774299	-4.2023935	3.6705640	C	2.0225790	-3.4834304	0.6829315
C	0.5632383	-5.4684950	3.4158056	C	1.5639705	-3.4093112	2.0117084
C	-5.0519102	4.8604063	-0.9637267	C	1.5942160	-2.1494854	2.6913327
C	-2.9502499	5.0937571	1.3261936	C	2.1357113	-1.0411248	2.0598870
C	-2.1457515	5.8065856	-1.6038909	C	1.0921400	-4.5785710	2.6861419
H	-5.3921403	5.9080585	-0.7977009	C	0.6897618	-5.5831711	3.2874547
H	-5.2275124	4.6064652	-2.0330640	C	-1.7045445	-1.0228024	-1.0502024
H	-5.6854025	4.1907377	-0.3398529	C	-1.9919084	0.1713835	-0.8982600
H	-3.2468569	6.1470229	1.5352347	Si	0.0911895	-7.0992846	4.1786787
H	-3.5598484	4.4286773	1.9779658	H	1.2155103	-2.0801781	3.7231366
H	-1.8816098	4.9721193	1.6118591	H	2.2044308	-0.0801844	2.5967184
H	-2.4220480	6.8756205	-1.4572451	H	3.3932517	0.9446350	0.7209209
H	-1.0668343	5.6905549	-1.3563979	H	4.6263399	0.6772740	-1.4391535
H	-2.2806219	5.5588751	-2.6805992	H	5.4354747	-0.7116701	-3.2431461
H	-2.6769312	-5.1208365	4.1582645	H	5.5371301	-2.9353512	-4.4018909
H	-2.8691134	-3.3334505	4.0359550	H	4.7514796	-5.2136326	-4.6661531
H	-2.4404286	-4.2944433	2.5736671	H	3.1052100	-7.0310785	-4.1325985
H	-0.5448532	-4.7027486	6.4791722	H	1.0205032	-7.7434670	-3.1387977
H	0.8908685	-3.6520307	6.1935488	H	-1.1433941	-7.2177725	-2.0007331
H	-0.7499034	-2.9191157	6.3336768	H	-2.7218815	-5.5440339	-1.1660670
H	0.2231172	-6.4139174	3.8966207	H	-3.3398640	-3.1690054	-0.6956649
H	0.4379960	-5.5757421	2.3150474	H	0.6708143	-1.9191557	-1.7939925
H	1.6485791	-5.3433807	3.6283450	H	2.0102268	-4.4625841	0.1859162
<b>H6DPP-I</b>				C	-2.2712763	1.5350584	-0.7271188
Total energy = -3231.847378 au				C	0.3821659	-6.8540815	6.0373217
C	-1.9709923	-4.7441764	-1.2778984	C	-1.7586339	-7.3181642	3.8171249
C	-0.6620613	-5.0983564	-1.7232004	C	1.0750084	-8.5893137	3.5375133
C	0.3508957	-4.0765341	-1.8427201	S	-0.9936023	2.7265971	-0.9477314
C	-0.0453774	-2.7330253	-1.6208637	C	-2.0837753	4.0602711	-0.5719925
C	-1.3557236	-2.3890921	-1.2279678	C	-3.3752033	3.5677100	-0.2937758
C	-2.3213232	-3.4285981	-1.0239029	C	-3.4799539	2.1669971	-0.3795279
C	-0.3688458	-6.4426663	-2.1229927	H	-4.4056987	1.6027237	-0.1953244
C	0.8289547	-6.7348603	-2.7359397	H	-4.2053777	4.2461686	-0.0348804
C	1.8558660	-5.7395939	-2.8826188	C	-1.7101474	5.4482323	-0.5470404
C	1.6977474	-4.4436279	-2.2869027	N	-0.4426535	5.9652451	-0.8115763
C	3.0114677	-6.0311181	-3.6776726	C	0.7652169	5.2454545	-1.1716774
C	3.9298887	-5.0407887	-3.9511747	H	0.6431392	4.6943105	-2.1296156
C	3.8618518	-3.7780115	-3.2788094	H	1.0748783	4.5401982	-0.3698290
C	2.8445817	-3.5424621	-2.2840070	H	1.5581010	6.0117720	-1.2985809
C	4.8049171	-2.7487918	-3.5986776	C	-0.4186707	7.4024632	-0.6890422
C	4.7659159	-1.5357583	-2.9459150	O	0.6088473	8.0670813	-0.8801272
C	3.9277330	-1.3634009	-1.7969329	C	-1.7800395	7.7478195	-0.3262482
C	3.0564055	-2.4222216	-1.3736246	C	-2.5468435	6.5492299	-0.2463144
C	4.0078517	-0.1438007	-1.0397591	C	-3.9072416	6.8956367	0.1183262
C	3.3424550	-0.0010119	0.1561925	O	-4.9349497	6.2323120	0.3102213
C	2.6515942	-1.1174825	0.7326805	N	-3.8816984	8.3345252	0.2419317

C	-5.0885710	9.0553760	0.6031411	C	3.0640345	-2.7644218	1.6082586
H	-5.8839878	8.2908627	0.7237407	C	3.0552911	-1.5029700	2.2851195
H	-5.3927106	9.7675540	-0.1946103	C	3.5711917	-0.3823364	1.6539940
H	-4.9663049	9.6008196	1.5643280	C	2.6042433	-3.9430084	2.2743302
C	-2.6151927	8.8485155	-0.0210230	C	2.2014173	-4.9559722	2.8609348
C	-2.2353905	10.2381005	0.0155003	C	-0.3352927	-0.6200370	-1.3836171
C	-0.9463828	10.7282723	-0.2538570	C	-0.7918134	0.5114984	-1.1752181
H	-0.1164667	10.0530175	-0.5213720	Si	1.5754489	-6.4804969	3.7176347
C	-0.8476119	12.1392600	-0.1435617	H	2.6654675	-1.4410177	3.3132355
H	0.0795009	12.7065990	-0.3163601	H	3.6101131	0.5818697	2.1878334
C	-2.0510217	12.7362506	0.2082186	H	4.7708824	1.6375922	0.3167073
H	-2.2675010	13.8029727	0.3632991	H	6.0110600	1.4071888	-1.8438494
S	-3.3175973	11.5792748	0.4083985	H	6.8644732	0.0519261	-3.6422954
H	0.0320424	-7.7474290	6.6033339	H	7.0588208	-2.1713522	-4.7911123
H	1.4630031	-6.7074180	6.2587130	H	6.3818082	-4.4756002	-5.0400948
H	-0.1718990	-5.9666381	6.4172642	H	4.8190035	-6.3654440	-4.5021224
H	0.7371700	-9.5217851	4.0447837	H	2.7776098	-7.1700525	-3.5201593
H	0.9330289	-8.7219973	2.4416073	H	0.5853610	-6.7528787	-2.3884747
H	2.1637595	-8.4653014	3.7323597	H	-1.0697146	-5.1740470	-1.5499393
H	-2.1459840	-8.2268637	4.3322424	H	-1.8097129	-2.8397189	-1.0555562
H	-2.3445539	-6.4421508	4.1747872	H	2.1180544	-1.3632056	-2.1740954
H	-1.9423902	-7.4346761	2.7258182	H	3.5584753	-3.8120385	-0.2068273

#### H6DPP-II

Total energy = -3231.847271 au

C	-0.3641084	-4.3338630	-1.6608382	C	1.8319833	-6.2639053	5.5846070
C	0.9597900	-4.6122659	-2.1135905	C	-0.2697582	-6.6716542	3.3172071
C	1.9157922	-3.5359859	-2.2344910	C	2.5569246	-7.9710057	3.0738479
C	1.4480046	-2.2156017	-2.0020804	S	-3.0498849	1.8951480	-0.4648050
C	0.1242014	-1.9486272	-1.5949598	C	-2.9527916	3.6501517	-0.3228832
C	-0.7818077	-3.0421842	-1.3942710	C	-1.6468795	4.0886201	-0.6232791
C	1.3199387	-5.9400258	-2.5120991	C	-0.7590827	3.0477451	-0.9546934
C	2.5318675	-6.1717592	-3.1214013	H	0.2983963	3.1964365	-1.2174217
C	3.5051817	-5.1246218	-3.2680095	H	-1.3778775	5.1577595	-0.5892167
C	3.2804717	-3.8340216	-2.6795769	C	-4.0455456	4.5073573	0.0509036
C	4.6762795	-5.3671941	-4.0560961	N	-5.3474651	4.1003709	0.3402954
C	5.5479748	-4.3371493	-4.3319305	C	-5.8947412	2.7560130	0.3268717
C	5.4165579	-3.0753987	-3.6677814	H	-5.3899521	2.1007835	1.0699747
C	4.3849878	-2.8791230	-2.6782313	H	-5.8281483	2.2971907	-0.6837041
C	6.3171588	-2.0100970	-3.9912205	H	-6.9645622	2.8539561	0.6058403
C	6.2279010	-0.7974809	-3.3438085	C	-6.1911948	5.2195912	0.6823717
C	5.3813282	-0.6561027	-2.1972659	O	-7.3870589	5.0835953	0.9741814
C	4.5484031	-1.7456931	-1.7725098	C	-5.3101018	6.3673307	0.5844835
C	5.4198672	0.5670928	-1.4428641	C	-4.0146105	5.9148143	0.1992262
C	4.7509961	0.6900219	-0.2468694	C	-3.1340827	7.0639305	0.1068292
C	4.0953006	-0.4473292	0.3294489	O	-1.9394031	7.2024431	-0.1857849
C	4.0270491	-1.6884730	-0.4045973	N	-3.9797018	8.1829170	0.4556904
C	3.5383704	-2.8304121	0.2846500	C	-3.4361389	9.5286043	0.4764267
				H	-2.3668642	9.4378026	0.1937050

H	-3.5023637	9.9797022	1.4905459	C	3.4305586	2.2243132	0.9844465
H	-3.9472742	10.1871126	-0.2593916	C	2.6536731	-1.4099243	1.3490153
C	-5.2789320	7.7732724	0.7409900	C	2.2947568	-2.4806463	1.8556358
C	-6.3769562	8.6257252	1.1219554	C	-0.4382882	2.0141212	-2.1579101
C	-7.6804953	8.1832091	1.4037026	C	-0.9085894	3.1391607	-1.9466363
H	-7.9516671	7.1156520	1.3494621	C	1.8851440	-3.7071892	2.3993482
C	-8.5676686	9.2340579	1.7519421	H	2.5820394	1.0110675	2.5657516
H	-9.6282610	9.0854869	2.0055778	H	3.4152586	3.1515659	1.5812359
C	-7.9552631	10.4802085	1.7397663	H	4.5188049	4.3913403	-0.2105852
H	-8.3951493	11.4622247	1.9653789	H	5.7646072	4.3776846	-2.3797609
S	-6.2873638	10.3818065	1.3026207	H	6.6835195	3.1970782	-4.2707072
H	1.4576361	-7.1584382	6.1327609	H	6.9984511	1.0701826	-5.5661373
H	2.9100579	-6.1353618	5.8294348	H	6.4530996	-1.2557207	-5.9613054
H	1.2827372	-5.3729467	5.9632807	H	5.0058427	-3.2624107	-5.5375127
H	2.2013931	-8.9062367	3.5634811	H	3.0095762	-4.2433220	-4.5966565
H	2.4335538	-8.0892208	1.9740336	H	0.8049509	-4.0133037	-3.4383029
H	3.6431767	-7.8602561	3.2895992	H	-0.9369400	-2.5704595	-2.5144423
H	-0.6817704	-7.5783193	3.8163892	H	-1.8051082	-0.3050061	-1.9155626
H	-0.8488876	-5.7894489	3.6706842	H	2.0412174	1.4317787	-2.9416782
H	-0.4332936	-6.7752212	2.2214164	H	3.6099176	-1.0668072	-1.1056294
<b>H6(DPP)<sub>2</sub>-I</b>				C	-1.4500188	4.4094984	-1.7017185
Total energy = -4494.692393 au				S	2.0240467	-5.1849011	1.4520910
C	-0.2780504	-1.6887762	-2.5823317	C	1.3419113	-6.1600955	2.7533755
C	1.0588244	-1.8731817	-3.0460421	C	1.0312402	-5.3435947	3.8599723
C	1.9549340	-0.7425522	-3.1077462	C	1.3333569	-3.9831240	3.6647083
C	1.4175084	0.5372054	-2.8133097	H	1.1606310	-3.1965418	4.4136085
C	0.0790486	0.7138018	-2.4048768	H	0.5906363	-5.7646007	4.7794001
C	-0.7662927	-0.4349578	-2.2569568	C	1.1295050	-7.5808564	2.6935984
C	1.4922040	-3.1548107	-3.5172006	N	1.4302377	-8.4135247	1.6165689
C	2.7125206	-3.2840168	-4.1409646	C	2.0161618	-8.0545276	0.3380157
C	3.6269830	-2.1784803	-4.2284729	H	3.0298806	-7.6147161	0.4614454
C	3.3326921	-0.9404925	-3.5645640	H	1.3674966	-7.3488533	-0.2256653
C	4.8071647	-2.3036416	-5.0308163	H	2.1035883	-8.9981636	-0.2398327
C	5.6168950	-1.2093299	-5.2440623	C	1.0848905	-9.7867038	1.8934397
C	5.4177657	-0.0005310	-4.5024725	O	1.2685330	-10.6950880	1.0718839
C	4.3808341	0.0726473	-3.5023770	C	0.5403256	-9.7486751	3.2373162
C	6.2532170	1.1345921	-4.7559395	C	0.5771945	-8.4027374	3.7047363
C	6.0982754	2.2946153	-4.0287508	C	0.0304038	-8.3659668	5.0477210
C	5.2507113	2.3111620	-2.8739589	O	-0.1531269	-7.4588718	5.8700752
C	4.4814444	1.1507699	-2.5243685	N	-0.3175950	-9.7408355	5.3224738
C	5.2224857	3.4801623	-2.0380230	C	-0.9069541	-10.1017896	6.5987943
C	4.5497987	3.4844558	-0.8369036	H	-0.9921857	-9.1604640	7.1803140
C	3.9582627	2.2777052	-0.3404961	H	-0.2627141	-10.8135259	7.1597074
C	3.9584414	1.0866809	-1.1570374	H	-1.9215619	-10.5382034	6.4709699
C	3.5342275	-0.1233012	-0.5495288	C	-0.0159920	-10.5702951	4.2462289
C	3.0528664	-0.1721642	0.7754404	C	-0.2342241	-11.9933146	4.1810864
C	2.9754833	1.0395033	1.5377191	C	0.0777713	-12.8072730	3.0790242



H	0.5267116	-12.3902497	2.1620599	C	1.1325930	-3.7615430	-3.8032857
C	-0.2423248	-14.1745141	3.2818912	C	2.1669511	-2.7679065	-3.9025763
H	-0.0724386	-14.9641193	2.5343391	C	2.0122754	-1.4990723	-3.2519777
C	-0.7972889	-14.4165912	4.5315454	C	3.3283248	-3.0293361	-4.6997215
H	-1.1375574	-15.3715861	4.9570901	C	4.2575485	-2.0348203	-4.9181120
S	-0.9344312	-12.9755568	5.4732542	C	4.1923821	-0.8037869	-4.1891534
S	-3.1386384	4.5816744	-1.2325264	C	3.1650585	-0.6082814	-3.1967376
C	-2.9972132	6.3362650	-1.1288418	C	5.1463337	0.2335441	-4.4446783
C	-1.6849414	6.7375906	-1.4519047	C	5.1083942	1.4128499	-3.7319624
C	-0.8266332	5.6696053	-1.7709674	C	4.2569987	1.5348434	-2.5860835
H	0.2306856	5.7864622	-2.0498068	C	3.3733905	0.4623658	-2.2300078
H	-1.3902932	7.8004019	-1.4424310	C	4.3321123	2.7119402	-1.7638251
C	-4.0609379	7.2310430	-0.7617416	C	3.6488678	2.7967355	-0.5710377
N	-5.3725957	6.8720026	-0.4562344	C	2.9464841	1.6560238	-0.0620891
C	-5.9625690	5.5456929	-0.4466736	C	2.8443806	0.4606623	-0.8645920
H	-5.4780949	4.8869449	0.3068711	C	2.3281779	-0.7054083	-0.2437603
H	-5.9115310	5.0684498	-1.4496197	C	1.8594067	-0.7041480	1.0865661
H	-7.0285135	5.6812800	-0.1686939	C	1.8721990	0.5208621	1.8316053
C	-6.1761687	8.0246832	-0.1275720	C	2.4142567	1.6610616	1.2622043
O	-7.3736615	7.9338644	0.1746171	C	1.4089386	-1.9135876	1.6813239
C	-5.2580782	9.1411474	-0.2515136	C	1.0371224	-2.9745570	2.1987114
C	-3.9818808	8.6386519	-0.6385107	C	-1.3844711	1.8989059	-1.9434993
C	-3.0635550	9.7549086	-0.7577417	C	-1.6787260	3.0907743	-1.7861450
O	-1.8669398	9.8475143	-1.0624575	C	0.6309777	-4.1996079	2.7481921
N	-3.8668292	10.9074023	-0.4227601	H	1.4839399	0.5348309	2.8617132
C	-3.2765623	12.2333831	-0.4324758	H	2.4730232	2.5935367	1.8479566
H	-2.2148293	12.0997300	-0.7266939	H	3.6966968	3.7114413	0.0424547
H	-3.3140916	12.7044128	0.5740186	H	4.9606435	3.5496152	-2.1094700
H	-3.7740590	12.8965612	-1.1733503	H	5.7884476	2.2445829	-3.9791634
C	-5.1770774	10.5477870	-0.1202290	H	5.8880241	0.0826593	-5.2466804
C	-6.2406575	11.4452713	0.2537906	H	5.0863645	-2.1827002	-5.6303037
C	-7.5564017	11.0549253	0.5549481	H	3.4201988	-4.0080197	-5.1988702
H	-7.8660439	9.9968674	0.5231416	H	1.3186112	-4.7533229	-4.2480060
C	-8.4023488	12.1432904	0.8908020	H	-0.8440382	-4.2638008	-3.0911056
H	-9.4652127	12.0378386	1.1563170	H	-2.4164608	-2.6135352	-2.1902814
C	-7.7460179	13.3663626	0.8496736	H	-3.0232364	-0.2526977	-1.6417446
H	-8.1483466	14.3677092	1.0602382	H	0.9978420	1.0120518	-2.6840762
S	-6.0868089	13.2000705	0.4002436	H	2.3287788	-1.6576769	-0.7909212
<b>H6(DPP)<sub>2</sub>-II</b>				C	-1.9677516	4.4526801	-1.6172558
Total energy = -4494.692156 au				S	0.7615708	-5.6757376	1.7970391
C	-1.6608127	-1.8147956	-2.2719114	C	0.1068717	-6.6551862	3.1086413
C	-0.3527700	-2.1603232	-2.7267807	C	-0.1909053	-5.8413466	4.2204362
C	0.6657380	-1.1405341	-2.8029144	C	0.1007749	-4.4790038	4.0218558
C	0.2760209	0.1971841	-2.5387630	H	-0.0627683	-3.6942255	4.7746960
C	-1.0351885	0.5355861	-2.1442929	H	-0.6148979	-6.2659125	5.1458266
C	-2.0047776	-0.5064872	-1.9746848	C	-0.1004904	-8.0765919	3.0505085
C	-0.0650040	-3.4888429	-3.1803837	N	0.2004870	-8.9094303	1.9739718

C	0.7931139	-8.5518691	0.6979762	C	-2.3566845	11.7634885	-0.9039229
H	1.8023464	-8.1038509	0.8276533	C	-1.9852983	13.1553075	-0.8635967
H	0.1443256	-7.8535902	0.1253066	C	-0.7009193	13.6550447	-1.1376522
H	0.8925657	-9.4970292	0.1245024	H	0.1321961	12.9859743	-1.4114083
C	-0.1432074	-10.2823293	2.2519775	C	-0.6115326	15.0664059	-1.0241918
O	0.0410475	-11.1913853	1.4311599	H	0.3105158	15.6411162	-1.2001322
C	-0.6866478	-10.2444180	3.5963117	C	-1.8176692	15.6539002	-0.6654751
C	-0.6489183	-8.8985011	4.0633996	H	-2.0406388	16.7187095	-0.5070256
C	-1.1962651	-8.8605211	5.4063428	S	-3.0751579	14.4877145	-0.4621537
O	-1.3770478	-7.9539100	6.2293885	<b>H6(DPP)<sub>2</sub>-III</b>			
N	-1.5468496	-10.2354646	5.6808446	Total energy = -4494.691988 au			
C	-2.1381821	-10.5941344	6.9573641	C	-0.0177611	-2.3445755	-3.5469588
H	-2.2145824	-9.6527439	7.5403215	C	1.3044891	-2.6262768	-4.0025675
H	-1.4994161	-11.3124146	7.5161237	C	2.2690292	-1.5558708	-4.1083475
H	-3.1565863	-11.0215448	6.8295237	C	1.8101063	-0.2353218	-3.8599353
C	-1.2459481	-11.0650961	4.6044711	C	0.4870904	0.0358939	-3.4527641
C	-1.4682343	-12.4873509	4.5379881	C	-0.4270140	-1.0533028	-3.2651461
C	-1.1574429	-13.3006838	3.4351268	C	1.6525935	-3.9506162	-4.4218874
H	-0.7065463	-12.8837975	2.5190652	C	2.8617847	-4.1823829	-5.0361013
C	-1.4812536	-14.6672685	3.6365998	C	3.8438485	-3.1415492	-5.1661547
H	-1.3128940	-15.4568616	2.8889646	C	3.6314006	-1.8575279	-4.5583391
C	-2.0376197	-14.9092625	4.8857812	C	5.0097444	-3.3834959	-5.9614238
H	-2.3801841	-15.8638136	5.3108164	C	5.8902617	-2.3580476	-6.2241464
S	-2.1721731	-13.4688109	5.8286218	C	5.7725745	-1.1055192	-5.5409437
S	-0.6973780	5.6528715	-1.8350071	C	4.7436242	-0.9108187	-4.5473020
C	-1.7996219	6.9801509	-1.4722884	C	6.6856136	-0.0478918	-5.8528851
C	-3.0885477	6.4791492	-1.1988678	C	6.6108688	1.1582659	-5.1929628
C	-3.1828462	5.0773491	-1.2795195	C	5.7649277	1.2970078	-4.0460152
H	-4.1057233	4.5065151	-1.0996484	C	4.9182661	0.2131703	-3.6312665
H	-3.9244266	7.1525450	-0.9460666	C	5.8205007	2.5132727	-3.2828147
C	-1.4353583	8.3705044	-1.4489741	C	5.1512995	2.6368877	-2.0868864
N	-0.1733008	8.8960363	-1.7225175	C	4.4787479	1.5056660	-1.5218184
C	1.0347191	8.1854505	-2.0998936	C	4.3954288	0.2681822	-2.2627307
H	0.8990755	7.6233424	-3.0493539	C	3.8910618	-0.8702179	-1.5804106
H	1.3698157	7.4915555	-1.2983461	C	3.4132141	-0.8005128	-0.2552083
H	1.8168391	8.9584450	-2.2507628	C	3.4181727	0.4610255	0.4272601
C	-0.1574965	10.3327710	-1.5965108	C	3.9512170	1.5740727	-0.1981389
O	0.8640321	11.0044760	-1.7947612	C	2.9361435	-1.9545616	0.4233448
C	-1.5179834	10.6689400	-1.2215829	C	2.5094364	-2.9231790	1.0649175
C	-2.2769913	9.4654120	-1.1401527	C	0.0370658	1.3661602	-3.2337829
C	-3.6370704	9.8014531	-0.7631679	C	-0.4093066	2.5018042	-3.0267466
O	-4.6592539	9.1318011	-0.5682477	C	2.0075973	-3.9808160	1.8379236
N	-3.6186135	11.2410762	-0.6324677	H	3.0251864	0.5245482	1.4538006
C	-4.8265816	11.9529843	-0.2561503	H	4.0016824	2.5364875	0.3377834
H	-5.6147990	11.1815344	-0.1295604	H	5.1844237	3.5790429	-1.5151772
H	-5.1445039	12.6656218	-1.0482702	H	6.4258820	3.3469195	-3.6760382
H	-4.6971060	12.4964948	0.7051962	H	7.2574797	2.0034995	-5.4812644

H	7.4260728	-0.2097629	-6.6536215	C	-2.4262960	-9.1921181	10.0880686
H	6.7190564	-2.4929500	-6.9386838	H	-2.7523977	-8.7751918	11.0530715
H	5.1405965	-4.3758397	-6.4235432	C	-2.5517027	-10.5351987	9.7583284
H	3.0976186	-5.1750324	-5.4543012	H	-2.9685805	-11.3535758	10.3627947
H	0.9102410	-4.7582546	-4.3112703	S	-1.9496349	-10.8760234	8.1760774
H	-0.7284029	-3.1820776	-3.4487150	S	-2.6627441	3.8942573	-2.3265134
H	-1.4544892	-0.8480141	-2.9265041	C	-2.5620321	5.6491550	-2.1929664
H	2.4856611	0.6147586	-4.0226522	C	-1.2541997	6.0837557	-2.4911167
H	3.9017145	-1.8497914	-2.0762353	C	-0.3678841	5.0389787	-2.8145138
C	-0.9646581	3.7650585	-2.7745872	H	0.6907478	5.1832459	-3.0746995
S	1.4041165	-3.6582582	3.4606564	H	-0.9833027	7.1524175	-2.4614043
C	0.9936681	-5.3535485	3.7162272	C	-3.6553560	6.5086021	-1.8262867
C	1.3257715	-6.1102325	2.5736448	N	-4.9586202	6.1042582	-1.5389606
C	1.8878606	-5.3491994	1.5310398	C	-5.5088579	4.7609901	-1.5500307
H	2.2085118	-5.7643001	0.5643574	H	-5.0091094	4.1070300	-0.8024485
H	1.1462776	-7.1978148	2.5324807	H	-5.4393795	4.2985173	-2.5587015
C	0.3992677	-5.8823863	4.9141676	H	-6.5796649	4.8617296	-1.2760019
N	0.0638406	-5.1554739	6.0559582	C	-5.8011912	7.2259991	-1.2022686
C	0.2363958	-3.7354601	6.3036140	O	-6.9979908	7.0930562	-0.9127957
H	-0.3498172	-3.1204098	5.5864035	C	-4.9180602	8.3722968	-1.3018338
H	1.3075462	-3.4400687	6.2630597	C	-3.6227516	7.9161015	-1.6831548
H	-0.1468005	-3.5502849	7.3287904	C	-2.7397276	9.0630727	-1.7771527
C	-0.5226307	-5.9982128	7.0693440	O	-1.5438632	9.1976395	-2.0685607
O	-0.8951803	-5.5566769	8.1649826	N	-3.5830306	10.1843404	-1.4328927
C	-0.5274436	-7.3189286	6.4699879	C	-3.0371449	11.5289965	-1.4153505
C	0.0369557	-7.2274669	5.1644435	H	-1.9681839	11.4359100	-1.6982840
C	0.0280882	-8.5483930	4.5651938	H	-3.1023074	11.9824871	-0.4021897
O	0.4004387	-8.9912038	3.4706358	H	-3.5477057	12.1867237	-2.1522970
N	-0.5629365	-9.3899869	5.5799515	C	-4.8835600	9.7784571	-1.1482942
C	-0.7407809	-10.8097889	5.3368926	C	-5.9790657	10.6348615	-0.7691883
H	-0.3499594	-11.0037630	4.3165621	C	-7.2846849	10.1978342	-0.4877488
H	-1.8140295	-11.0984586	5.3708978	H	-7.5606369	9.1313722	-0.5417837
H	-0.1660269	-11.4235747	6.0643167	C	-8.1675634	11.2526605	-0.1396769
C	-0.8972215	-8.6621010	6.7180995	H	-9.2290066	11.1091306	0.1138910
C	-1.5058622	-9.1848710	7.9154838	C	-7.5497473	12.4962513	-0.1518674
C	-1.8360179	-8.4251305	9.0505504	H	-7.9853180	13.4803281	0.0736012
H	-1.6412409	-7.3405221	9.0954411	S	-5.8823287	12.3906509	-0.5887833

## References

<sup>2.1</sup> (a) TURBOMOLE V6.6 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>, (b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.*

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1989, **162**, 165. (c) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.* 2014, **4**, 91.

<sup>2.2</sup> Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

<sup>2.3</sup> M. Srebro-Hooper, J. Autschbach, *Annu. Rev. Phys. Chem.* 2017, **68**, 399.

<sup>2.4</sup> (a) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098, (b) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822, (c) J. P. Perdew, *Phys. Rev. B* 1986, **34**, 7406.

<sup>2.5</sup> (a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* 1992, **97**, 2571, (b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* 1997, **97**, 119, (c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.

<sup>2.6</sup> (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 1372; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.

<sup>2.7</sup> (a) A. Klamt, G. J. Schuurmann, *J. Chem. Soc., Perkin Trans. 2* 1993, 799, (b) A. Klamt, *J. Phys. Chem.* 1996, **100**, 3349.

<sup>2.8</sup> J. Autschbach, T. Ziegler, S. J. A. van Gisbergen, E. J. Baerends, *J. Chem. Phys.* 2002, **116**, 6930.

<sup>2.9</sup> C. Adamo, V. Barone, *J. Chem. Phys.* 1999, **110**, 6158.

<sup>2.10</sup> (a) T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* 2004, **393**, 51, (b) J. Autschbach, M. Srebro, *Acc. Chem. Res.* 2014, **47**, 2592.

<sup>2.11</sup> (a) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999, (b) M. Cossi, V. Barone, *J. Chem. Phys.* **2001**, *115*, 4708.