

Supplementary Materials for

Distinct properties of the triplet pair state from singlet fission

M. Tuan Trinh, Andrew Pinkard, Andrew B. Pun, Samuel N. Sanders, Elango Kumarasamy, Matthew Y. Sfeir, Luis M. Campos, Xavier Roy, X.-Y. Zhu

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1. Transient absorption

1.1. Charge transfer excitation for $[\text{Fe}_8\text{O}_4]\text{-Pc}$

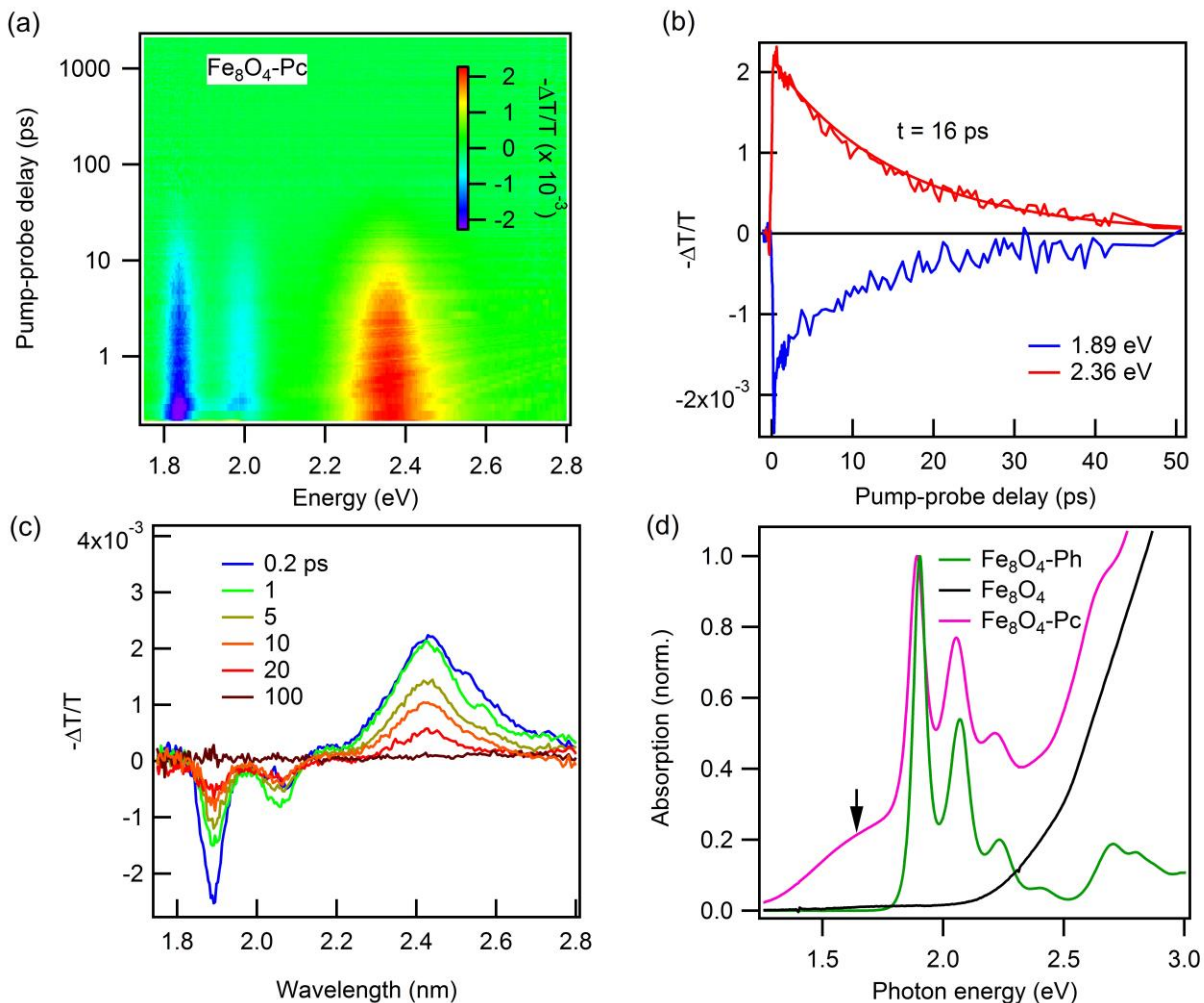


fig. S1. Transient absorption (TA) spectra and dynamics of $[\text{Fe}_8\text{O}_4]\text{-Pc}$. (a) 2D pseudocolor plot of TA ($-\Delta T/T$, T: transmission) as a function of pump-probe delay (Δt) and probe photon energy upon CT excitation of 1.65 eV (arrow in (d)). (b) Decay dynamics at probe photon energy of 1.89 eV (bleaching) and 2.36 eV (ESA). (c) TA spectra at several pump-probe delay. (d) Absorption spectra of TIPS-pentacene-phenol (Pc-Ph, green); $\text{Fe}_8\text{O}_4\text{pz}_{12}\text{Cl}_4$ cluster, i.e., $[\text{Fe}_8\text{O}_4]$ (black); and $[\text{Fe}_8\text{O}_4]\text{-Pc}$ (purple). Note that at this excitation energy, there is no absorbance by the $[\text{Fe}_8\text{O}_4]$ only.

1.2. Transient absorption for the $[\text{Fe}_8\text{O}_4]$ cluster

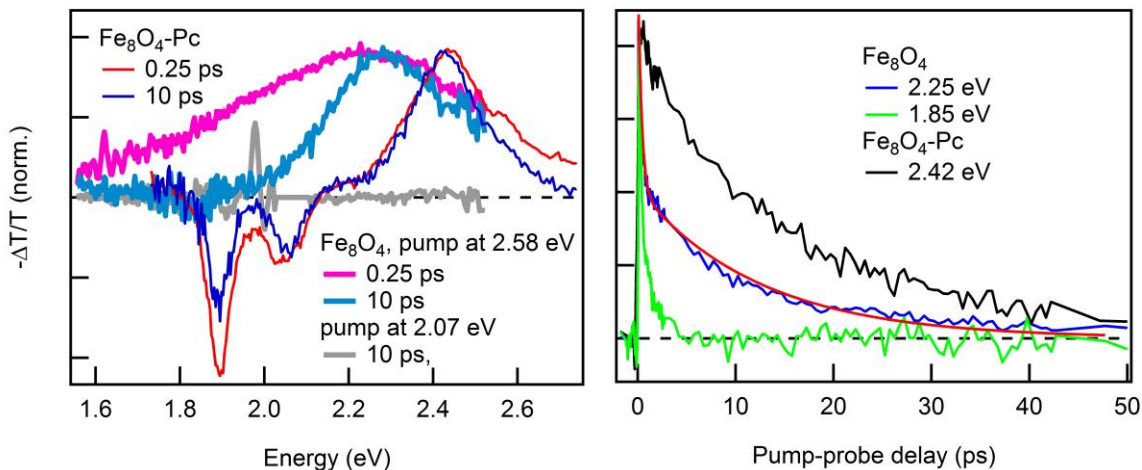


fig S2. Comparison between $\text{Fe}_8\text{O}_4\text{pz}_{12}\text{Cl}_4$ cluster only (pumped at 2.58 and 2.07 eV) and $[\text{Fe}_8\text{O}_4]\text{-Pc}$ (pumped at 1.65 eV). Left: The normalized spectra at 0.25 and 10 ps for both samples, the data for $\text{Fe}_8\text{O}_4\text{pz}_{12}\text{Cl}_4$ cluster above 2.53 eV was omitted due to strong scattering from the pump pulse. The grey curve is from the cluster pumped at 2.07 eV showing no pump-induced absorption signal. Right: Dynamics for the cluster at 1.85 and 2.25 eV. The biexponential fit to the dynamics at 2.25 eV (blue) gives the time constants of 0.36 (54 %) and 12.4 ps (46%). The dynamics for $[\text{Fe}_8\text{O}_4]\text{-Pc}$ decay mono-exponentially with a constant of 16 ps (black).

2. Triplet-sensitizing experiments

The triplet sensitizing experiment was carried out on the same setup as the femtosecond transient absorption setup except the white-light probe beams were generated by a supercontinuum laser from Leukos. The laser pulse width is < 1 ns runs at 2 kHz. The pump-probe delay was controlled electrically. A mixture of the compound and anthracene was dissolved in toluene and kept free from oxygen to avoid oxygen triplet quenching. Photoexcitation at 3.44 eV creates singlets in anthracene which undergo intersystem crossing to form triplets. The triplets in

anthracene subsequently transfer to pentacene molecules via diffusional collisions in time scale of $\sim 1\text{-}2\ \mu\text{s}$.

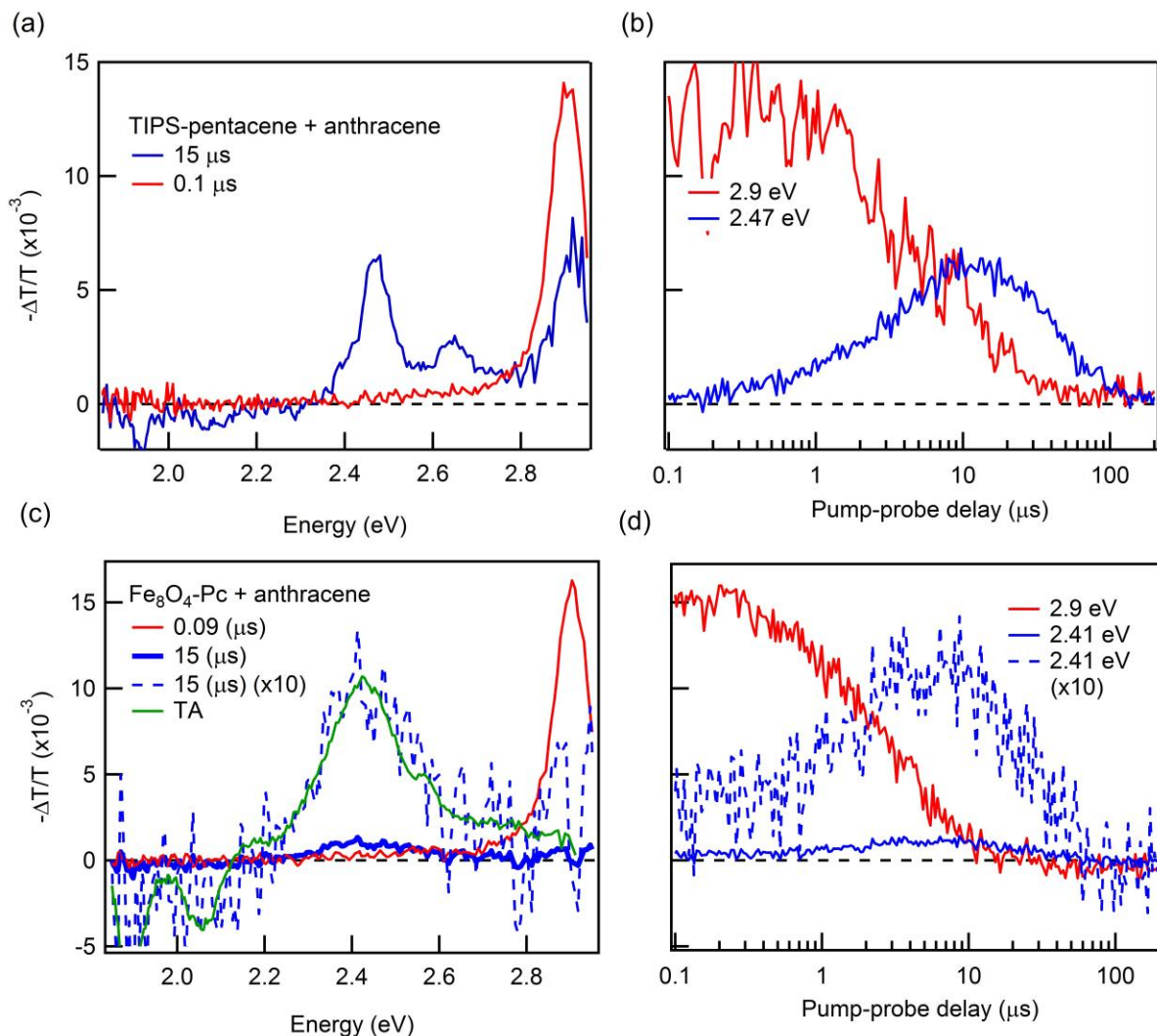


fig. S3. Triplet-sensitizing experiments. (a, b) Spectra and dynamics for the mixed solution of anthracene and TIPS-pentacene. (c,d) Mixed solution of Fe₈O₄-Pc and anthracene. The peaks at 2.47 (in a, b) and 2.41 eV (in c, d) are assigned to triplet absorption in pentacene, the peak at 2.9 eV is triplet absorption from anthracene. The TA spectrum for [Fe₈O₄]-Pc excited at 1.65 eV (Fig. 2 in the main text) was plotted in (c) for comparison. The molar concentration for anthracene is 50 mM, for TIPS-Pentacene is 15 μM , and for [Fe₈O₄]-Pc is 36 μM . Note that the small T1 signal observed from sensitization of [Fe₈O₄]-Pc may come from a small population of free TIPS-Pc molecules that has broken off the cluster from laser irradiation.

3. Compound synthesis

3.1 General

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar[®], Sigma-Aldrich[®], Acros organics[®], TCI America[®], Mallinckrodt[®], Strem Chemicals[®] and Oakwood[®] Products, and were used as received without further purification. Synthesis of **1**, Dibromo NODIPS Pentacene, **4**, **5** and Fe₈O₄pZ₁₂Cl₄ (Iron Oxo Cluster) were synthesized as previously reported. (11, 49, 60) Unless stated otherwise, reactions were conducted in oven-dried glassware under argon atmosphere. ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker 400 MHz (100 MHz for ¹³C) and on 500 MHz (125 MHz for ¹³C) spectrometers. Data from the ¹H-NMR and ¹³C spectroscopy are reported as chemical shift (δ ppm) with the corresponding integration values. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), m (multiplet) and virt (virtual).

The mass spectral data for the compounds were obtained from (1) XEVO G2-XS Waters[®] equipped with a QTOF detector with multiple inlet and ionization capabilities including electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric solids analysis probe (ASAP) or (2) a Bruker UltrafleXtreme MALDI TOF/TOF instrument using a dithranol matrix. The base peaks were usually obtained as [M]⁺ or [M+H]⁺ ions. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum 400 FTIR spectrometer using a PIKE ATR attachment

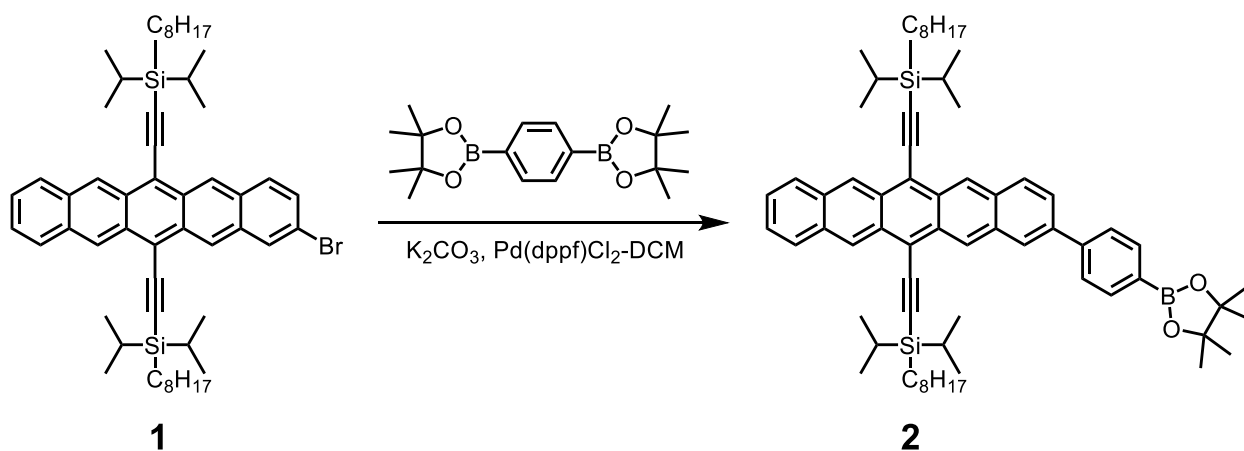
Absorption spectra were obtained on a Shimadzu UV 1800 UV-Vis spectrophotometer.

Anhydrous solvents were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). All reactions

were carried out under argon unless otherwise noted. Reactions and sample preparations requiring an inert atmosphere were carried out under nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox

3.2 Synthesis

fig. S4. Synthetic route for compound 2.



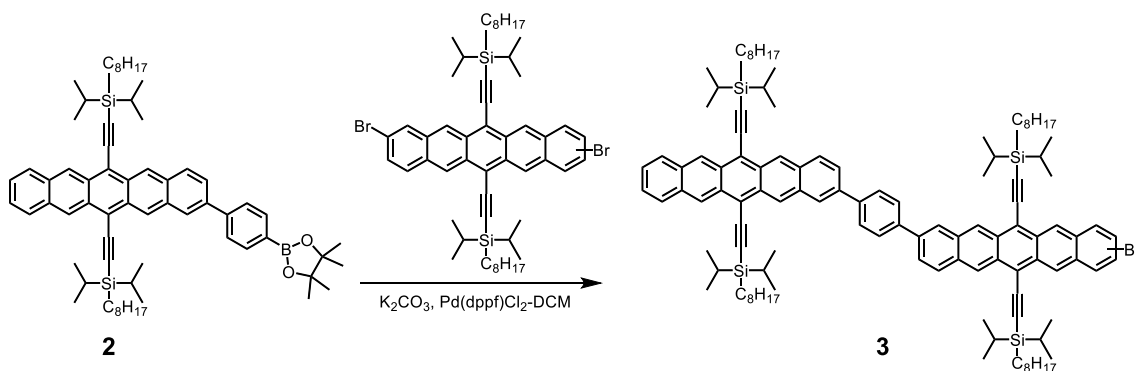
1 (1.5 g, 1.75 mmol), 1,4-Benzenediboronic acid bis(pinacol) ester (1.73 g, 5.25 mmol) and $Pd(dppf)Cl_2 \cdot DCM$ (71.1 mg, 0.09 mmol) were added to a reaction vial, followed by sequential vacuum and argon to degas the solids. K_2CO_3 (1.2 g, 8.75 mmol) was then dissolved in 4.5 mL H_2O and degassed. The solids were then dissolved in 45 mL of a mixture of 9:1 THF: K_2CO_3 in H_2O solution, and allowed to stir at 70 °C overnight in the dark. The reaction was then brought to room temperature and extracted with DCM and the combined organic layers were washed with DI water and brine, dried over sodium sulfate, filtered and concentrated. The crude was then purified by column chromatography using 25% to 50% DCM in hexanes as the eluent to obtain **2** as a deep blue solid (973 mg, 56.7% yield).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ ppm): 9.36 (s, 1H), 9.32 (s, 3H), 8.20 (s, 1H), 8.09 (d, 1H), 8.03-8.00 (m, 4H), 7.84 (d, 2H), 7.76 (d, 1H), 7.46-7.42 (m, 2H), 1.80 (m, 4H), 1.56 (m, 6H), 1.45-1.35 (m, 54H), 0.99 (m, 4H), 0.83 (m, 6H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ ppm): 143.47, 138.19, 136.40, 135.43, 132.39, 132.35, 132.32, 131.55, 130.93, 130.78, 130.69, 130.62, 129.34, 129.19, 128.68, 126.77, 126.54, 126.33, 126.29, 126.12, 126.02, 125.57, 118.44, 118.32, 107.66, 107.51, 104.54, 104.51, 83.89, 34.05, 34.02, 33.97, 31.97, 31.92, 29.50, 29.47, 29.39, 29.37, 25.01, 24.96, 24.92, 24.74, 22.64, 18.71, 18.44, 14.08, 14.06, 12.18, 10.47.

MS (ESI): Calculated $[\text{M}]^+$: 980.6505; Observed: 980.6499.

fig. S5. Synthetic route for compound 3.



2 (250 mg, 0.25 mmol), Dibromo NODIPS Pentacene (586 mg, 0.625 mmol) and $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{DCM}$ (10.2 mg, 0.013 mmol) were added to a reaction vial, followed by sequential vacuum and argon to degas the solids. K_2CO_3 (173 mg, 1.25 mmol) was then dissolved in 1.2 mL H_2O and degassed. The solids were then dissolved in 12 mL of a mixture of 9:1 THF: K_2CO_3 in H_2O solution, and allowed to stir at 70 °C overnight in the dark. The reaction was then brought to room temperature and extracted with DCM and the combined organic layers were washed with DI water and brine, dried over sodium sulfate, filtered and concentrated. The crude was then

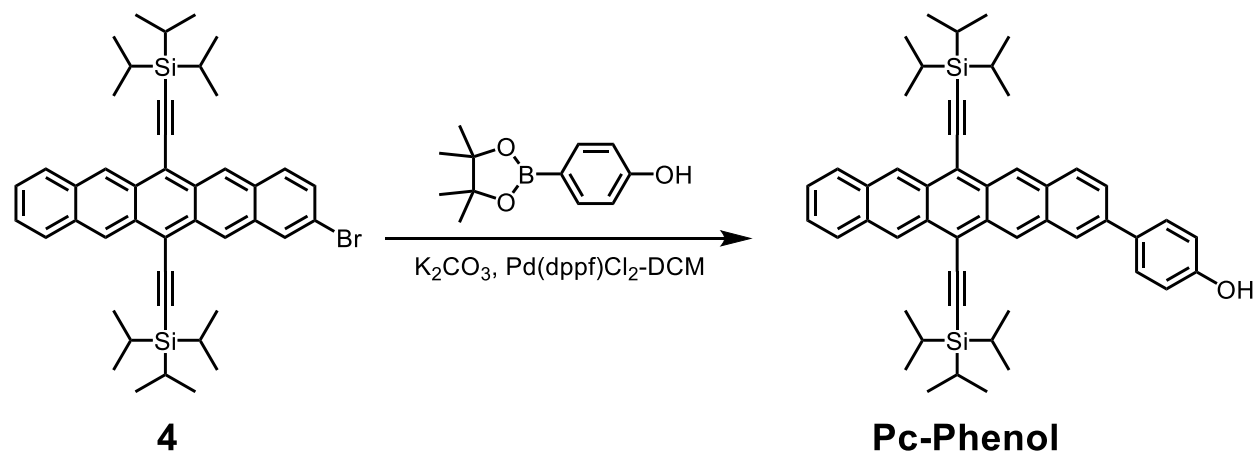
purified by column chromatography using 0% to 10% DCM in hexanes as the eluent to obtain **3** as a green solid (328 mg, 75.2% yield).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ ppm): 9.37-9.30 (m, 8H), 8.26 (s, 2H), 8.13 (t, 3H), 7.99 (m, 6H), 7.83-7.81 (m, 3H), 7.44-7.41 (m, 3H), 7.76 (d, 1H), 7.46-7.42 (m, 2H), 1.79-1.78 (m, 8H), 1.39-1.34 (m, 90H), 1.01-0.96 (m, 12H), 0.84-0.80 (m, 14H).

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ ppm): 140.03, 139.87, 137.85, 137.62, 132.46, 132.38, 132.33, 131.53, 131.23, 130.96, 130.82, 130.79, 130.75, 130.63, 130.42, 130.22, 129.49, 128.70, 127.73, 126.92, 126.70, 126.36, 126.29, 126.23, 126.20, 126.15, 126.07, 125.82, 125.76, 125.53, 120.39, 118.63, 118.49, 118.29, 108.11, 108.00, 107.91, 107.64, 107.54, 104.60, 104.53, 104.28, 34.07, 32.01, 31.98, 29.55, 29.51, 29.44, 29.41, 25.00, 22.69, 18.77, 18.49, 14.15, 14.12, 12.21, 12.18.

MS (ESI): Calculated $[\text{M}]^+$: 1711.9937; Observed: 1711.9988.

fig. S6. Synthetic route for compound Pc-Phenol.



4 (300 mg, 0.42 mmol), 4-Hydroxyphenylboronic acid pinacol ester (110 mg, 0.50 mmol) and $\text{Pd}(\text{dppf})\text{Cl}_2\cdot\text{DCM}$ (17.1 mg, 0.021 mmol) were added to a reaction vial, followed by sequential vacuum and argon to degas the solids. K_2CO_3 (577 mg, 4.2 mmol) was then dissolved in 1 mL

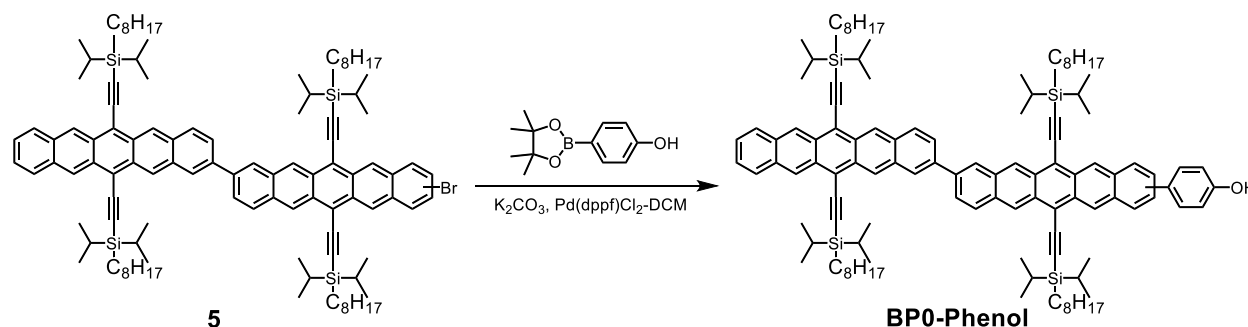
H₂O and degassed. The solids were then dissolved in 10 mL of a mixture of 9:1 THF:K₂CO₃ in H₂O solution, and allowed to stir at 70 °C overnight in the dark. The reaction was then brought to room temperature and extracted with DCM and the combined organic layers were washed with DI water and brine, dried over sodium sulfate, filtered and concentrated. The crude was then purified by column chromatography using 35% to 50% DCM in hexanes as the eluent to obtain **Pc-Phenol** as a teal solid (226 mg, 74.0% yield).

¹H-NMR (500 MHz, CDCl₃, δ ppm): 9.33 (s, 4H), 8.07 (t, 2H), 8.00 (m, 2H), 7.71 (m, 3H), 7.44 (m, 2H), 7.03 (d, 2H), 4.90 (s, 1H), 1.48-1.39 (m, 42H).

¹³C-NMR (125 MHz, CDCl₃, δ ppm): 155.58, 137.93, 133.74, 132.41, 129.42, 128.83, 128.71, 126.53, 126.18, 126.15, 116.04, 19.16, 11.86.

MS (ESI): Calculated [M]⁺: 730.4026; Observed: 730.4038.

fig. S7. Synthetic route for compound BP0-Phenol.



5 (100 mg, 0.06 mmol), 4-Hydroxyphenylboronic acid pinacol ester (16 mg, 0.07 mmol) and Pd(dppf)Cl₂·DCM (2.5 mg, 0.003 mmol) were added to a reaction vial, followed by sequential vacuum and argon to degas the solids. K₂CO₃ (84.3 mg, 0.61 mmol) was then dissolved in 1 mL H₂O and degassed. The solids were then dissolved in 10 mL of a mixture of 9:1 THF:K₂CO₃ in

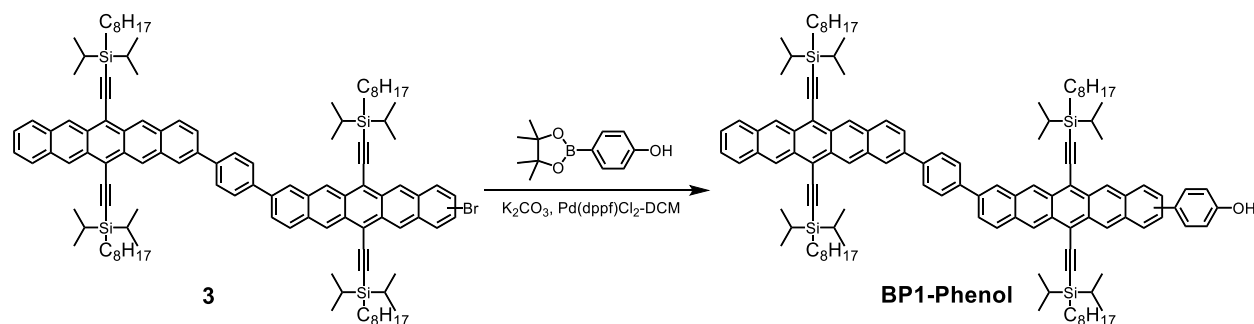
H₂O solution, and allowed to stir at 70 °C overnight in the dark. The reaction was then brought to room temperature and extracted with DCM and the combined organic layers were washed with DI water and brine, dried over sodium sulfate, filtered and concentrated. The crude was then purified by column chromatography using 50% to 75% DCM in hexanes as the eluent to obtain **BP0-Phenol** as a green solid (53 mg, 52.7% yield).

¹H-NMR (500 MHz, CDCl₃, δ ppm): 9.40 (s, 2H), 9.33 (m, 6H), 8.36 (s, 2H), 8.15 (d, 2H), 8.10 (s, 1H), 8.06 (d, 2H), 8.00 (m, 2H), 7.94 (m, 2H), 7.70 (m, 3H), 7.43 (m, 2H), 7.01 (d, 2H), 4.84 (s, 1H), 1.80 (m, 8H), 1.45-1.21 (m, 90H), 0.99 (m, 9H), 0.84 (m, 9H), 0.74 (m, 8H).

¹³C-NMR (125 MHz, CDCl₃, δ ppm): 155.47, 137.85, 133.60, 132.36, 131.60, 130.66, 129.61, 128.70, 128.57, 126.37, 126.20, 126.06, 125.95, 124.86, 115.90, 107.55, 104.53, 34.08, 34.03, 31.98, 31.91, 29.53, 29.47, 29.39, 29.37, 25.04, 24.97, 22.66, 22.61, 18.76, 18.74, 18.48, 14.10, 14.01, 12.21, 10.50.

MS (ESI): Calculated [M+H]⁺: 1649.0870; Observed: 1649.0900.

fig. S8. Synthetic route for compound BP1-Phenol.



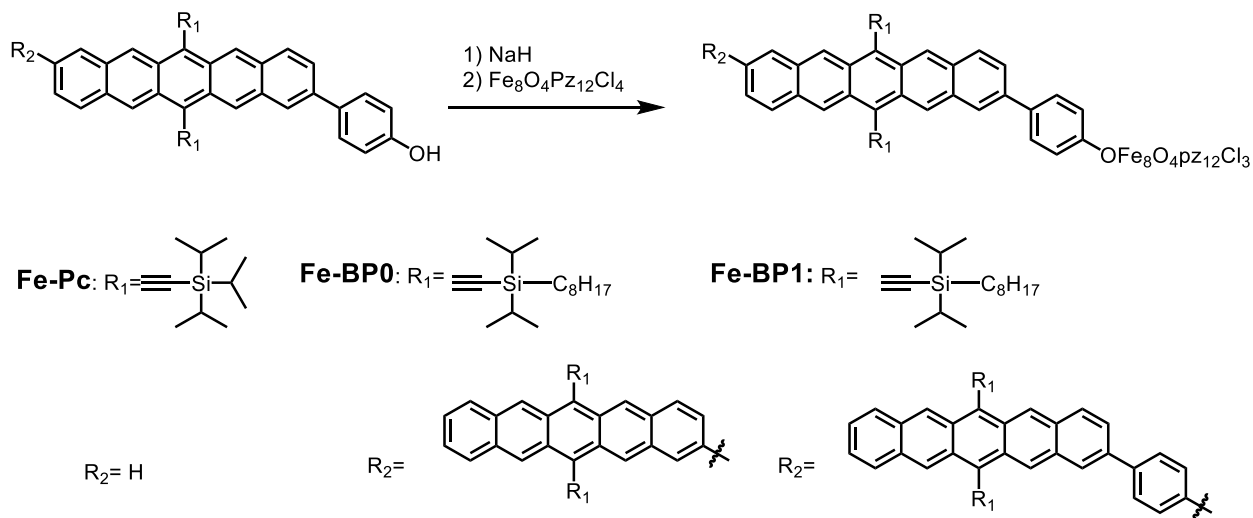
3 (325 mg, 0.2 mmol), 4-Hydroxyphenylboronic acid pinacol ester (50.6 mg, 0.23 mmol) and Pd(dppf)Cl₂·DCM (8.16 mg, 0.01 mmol) were added to a reaction vial, followed by sequential vacuum and argon to degas the solids. K₂CO₃ (263 mg, 1.9 mmol) was then dissolved in 1 mL H₂O and degassed. The solids were then dissolved in 10 mL of a mixture of 9:1 THF:K₂CO₃ in H₂O solution, and allowed to stir at 70 °C overnight in the dark. The reaction was then brought to room temperature and extracted with DCM and the combined organic layers were washed with DI water and brine, dried over sodium sulfate, filtered and concentrated. The crude was then purified by column chromatography using 50% DCM in hexanes as the eluent to obtain **BP1-Phenol** as a green solid (121 mg, 37.0% yield).

¹H-NMR (400 MHz, CDCl₃, δ ppm): 9.37 (s, 2H), 9.32 (d, 6H), 8.26 (s, 2H), 8.13-8.04 (m, 4H), 7.99 (m, 6H), 7.81 (d, 2H), 7.70 (m, 3H), 7.43 (m, 2H), 7.01 (d, 2H), 4.83 (s, 1H), 1.79 (m, 8H), 1.43-1.20 (m, 100H), 0.82 (m, 18H).

¹³C-NMR (125 MHz, CDCl₃, δ ppm): 155.59, 140.52, 140.13, 137.83, 133.72, 132.62, 132.52, 132.48, 131.69, 131.12, 130.91, 130.78, 129.61, 129.42, 128.84, 128.70, 127.87, 127.32, 126.82, 126.50, 126.32, 126.20, 125.95, 124.97, 118.64, 118.45, 116.03, 107.80, 107.68, 104.75, 34.23, 34.19, 32.14, 32.11, 29.67, 29.64, 29.59, 29.56, 29.53, 25.18, 25.13, 22.81, 18.91, 18.89, 18.86, 18.64, 18.62, 14.26, 14.23, 12.36, 10.65.

MS (ESI): Calculated [M+H]⁺: 1725.1184; Observed: 1725.1183

fig. S9. Synthetic route for compound [Fe₈O₄]-Pc, [Fe₈O₄]-BP0, and [Fe₈O₄]-BP1.



In a nitrogen-filled glovebox, Fe₈O₄pz₁₂Cl₄ (1 eq) was dissolved in approximately 10 mL of anhydrous THF. In a separate vial, NaH (10 eq) was suspended in THF to which **Pc**, **BP0**, or **BP1** Phenol (1 eq.) was added and stirred for about 1 h, turning the suspension from dark green to a dark violet. This mixture was then filtered through a syringe filter (0.2 mm PTFE) to give a dark violet solution. This solution was slowly added dropwise to the solution of Fe₈O₄pz₁₂Cl₄ and stirred for 16 h at room temperature. The solvent was then removed under vacuum. The residue was removed from the glovebox and purified via flash chromatography using a RediSep® Rf Reversed-phase C18 column and gradient elution (10% to 50% DCM in MeCN). Fractions containing the desired product were collected and concentrated to give the products as dark green solids.

Upon reaction of the sodium salt of Pc-PhOH with Fe₈O₄pz₁₂Cl₄, a chloride is displaced from the cluster, substituted with a Pc-PhO⁻, BP0-PhO⁻, and BP1-PhO⁻, giving rise to [Fe₈O₄]-Pc, [Fe₈O₄]-BP0, and [Fe₈O₄]-BP1, respectively. The high-spin Fe³⁺ centers of the cluster give rise to large

paramagnetic shifting and signal broadening of the resulting adducts, making complete characterization by NMR a challenge. However, the position of the aromatic protons of the pentacenes shifts from the usual 6-8 ppm region upon addition to the cluster. In the case of the simplest adduct, $[\text{Fe}_8\text{O}_4]\text{-Pc}$, upon treatment with anhydrous HCl, the aromatic resonances associate with the pentacene moiety return to the 6-8 ppm region, evidence that the pentacene moiety goes from being directly covalently linked to the cluster to the free Pc-PhOH and $\text{Fe}_8\text{O}_4\text{pz}_{12}\text{Cl}_4$ molecules. Mass spectrometry of the $[\text{Fe}_8\text{O}_4]\text{-Pc}$ adduct shows the molecular ion of the desired compound ($m/z = 2152$), as well as fragments corresponding to $\text{Fe}_8\text{O}_4\text{pz}_{12}\text{Cl}_3$ ($m/z = 1420$) and Pc-PhOH ($m/z = 730$). Taken in context of the NMR and IR data, we use this as evidence for formation of the desired product. The larger size of $[\text{Fe}_8\text{O}_4]\text{-BP0}$ and $[\text{Fe}_8\text{O}_4]\text{-BP1}$ fragment more quickly upon ionization into the BP0/BP1 and $\text{Fe}_8\text{O}_4\text{pz}_{12}\text{Cl}_4$, but the distinct electronic absorption and IR spectra, as well as the ability to separate the material from any remaining starting material using RP-chromatography, indicate that monosubstituted adducts have formed.

Fe-Pc: (15 mg, 20% yield)

MS (ESI): Calculated $[\text{M}]^+$: 2152.1179; Observed: 2152.1206

Fe-BP0: (23 mg, 22% yield)

Fe-BP1: (18 mg, 17% yield)

3.3. Infrared Spectrum

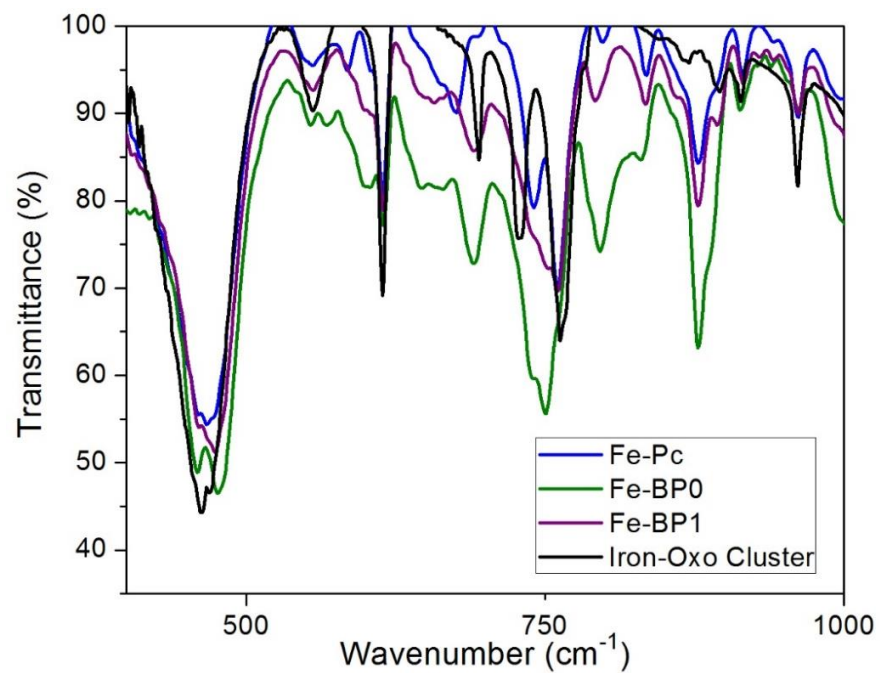


fig. S10. Infrared spectra. Infrared spectrum of the chloride terminated Iron-oxo cluster (black), Fe-Pc (blue), Fe-BP0 (green), Fe-BP1 (purple). The stretch peak at 460 cm⁻¹ corresponds to the Fe-O stretch of the cluster cubane structure. The persistence of this peak after the ligand exchange demonstrates the cluster remains intact

3.4. UV-Vis Spectra

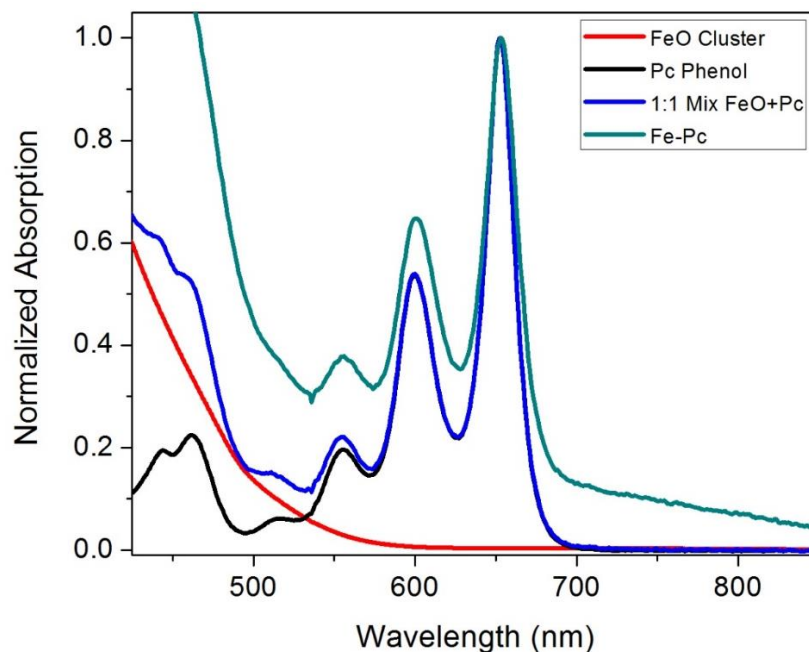


fig. S11. Absorption spectra. Normalized UV-Vis spectra of Pc-Phenol (black), Iron-Oxo cluster (red), a 1:1 mixture of the two in solution (blue) and the 1:1 adduct Fe-Pc (green).

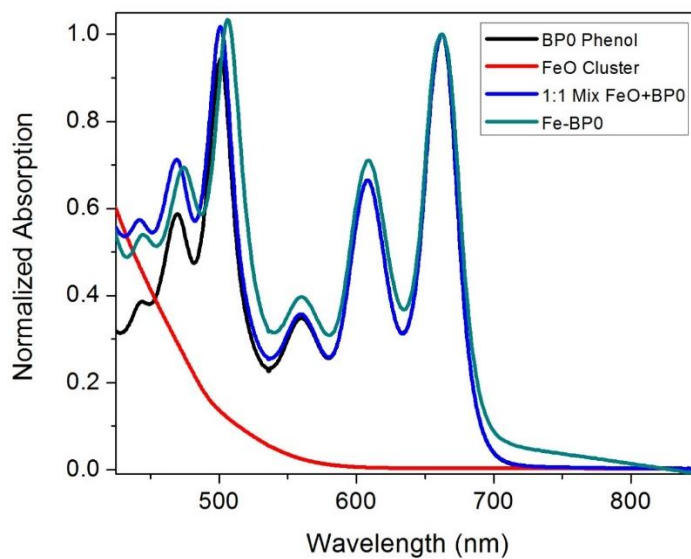


fig. S12. Normalized absorption spectra. Normalized UV-Vis spectra of BP0-Phenol (black), Iron-Oxo cluster (red), a 1:1 mixture of the two in solution (blue) and the 1:1 adduct Fe-BP0 (green).

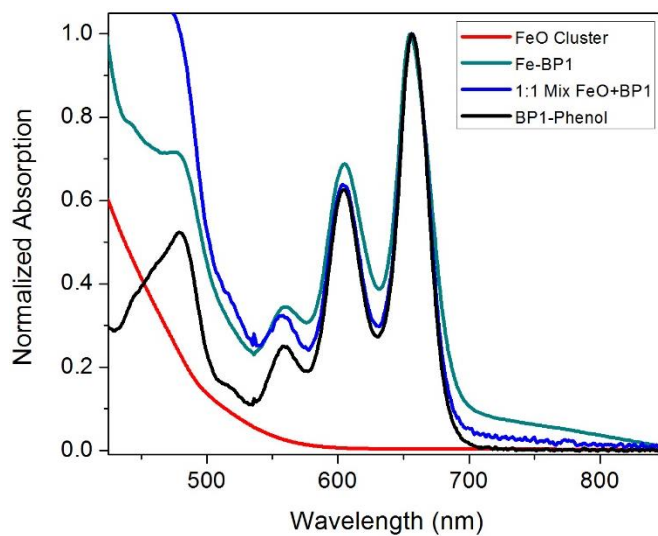
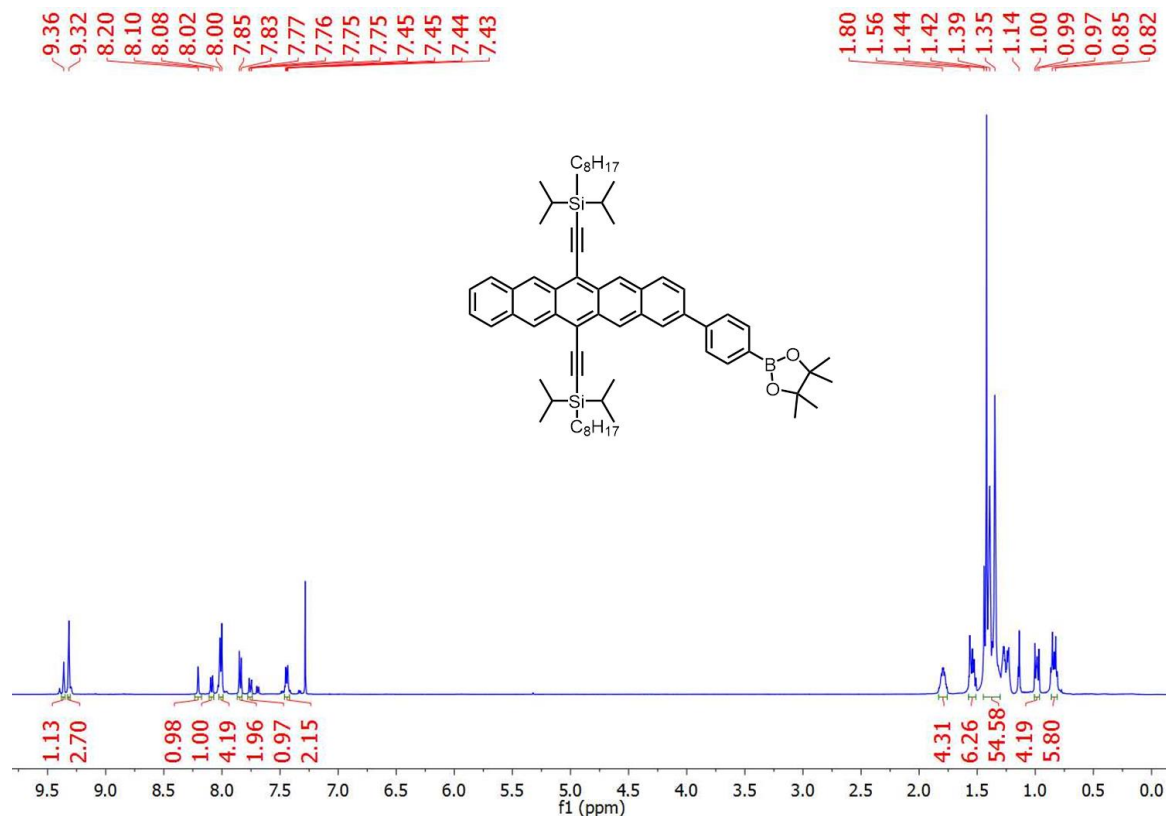
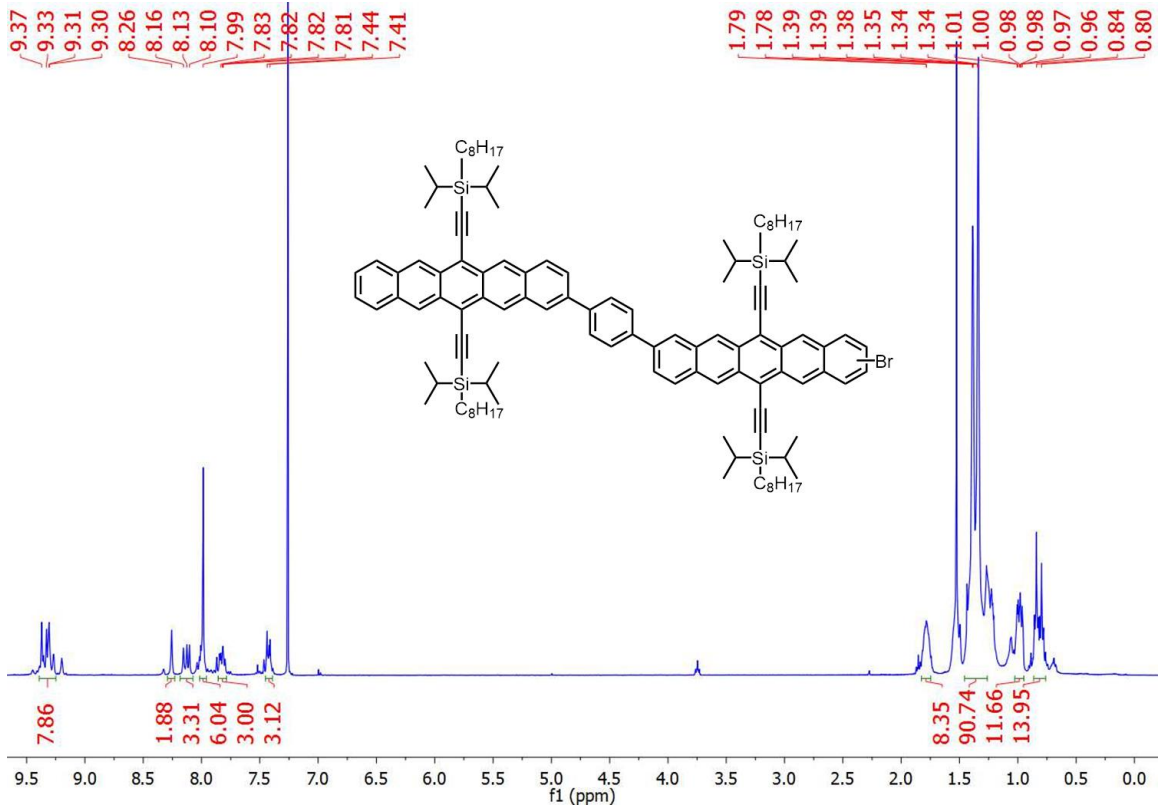
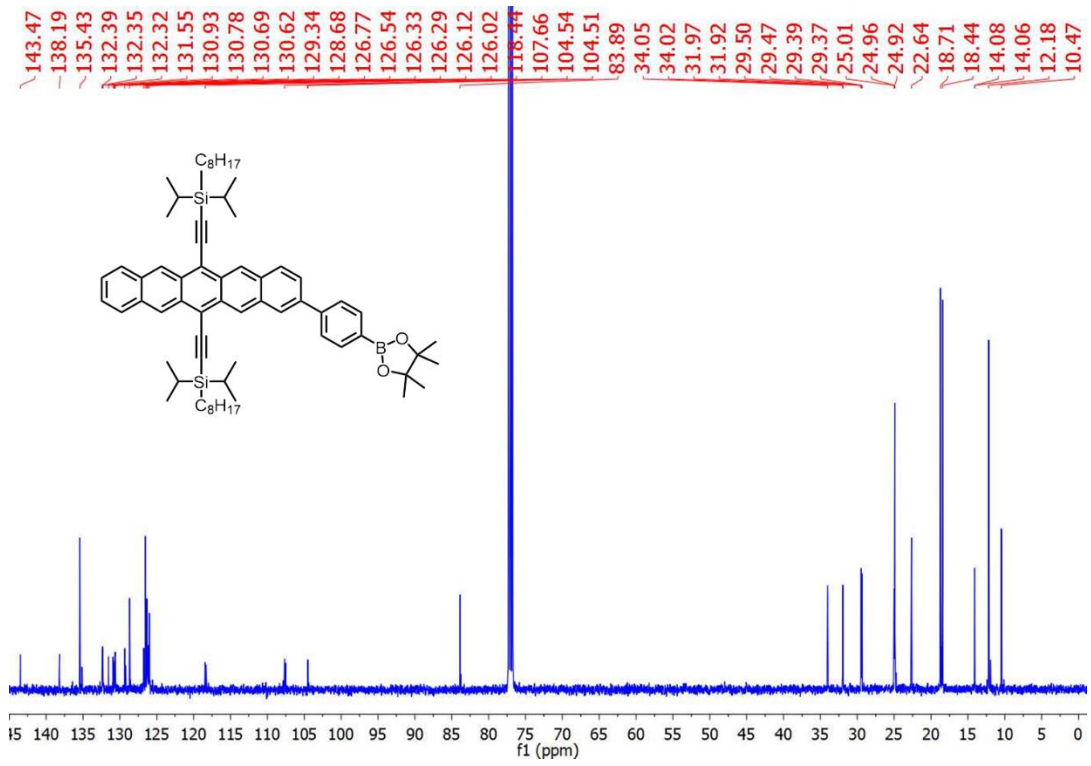


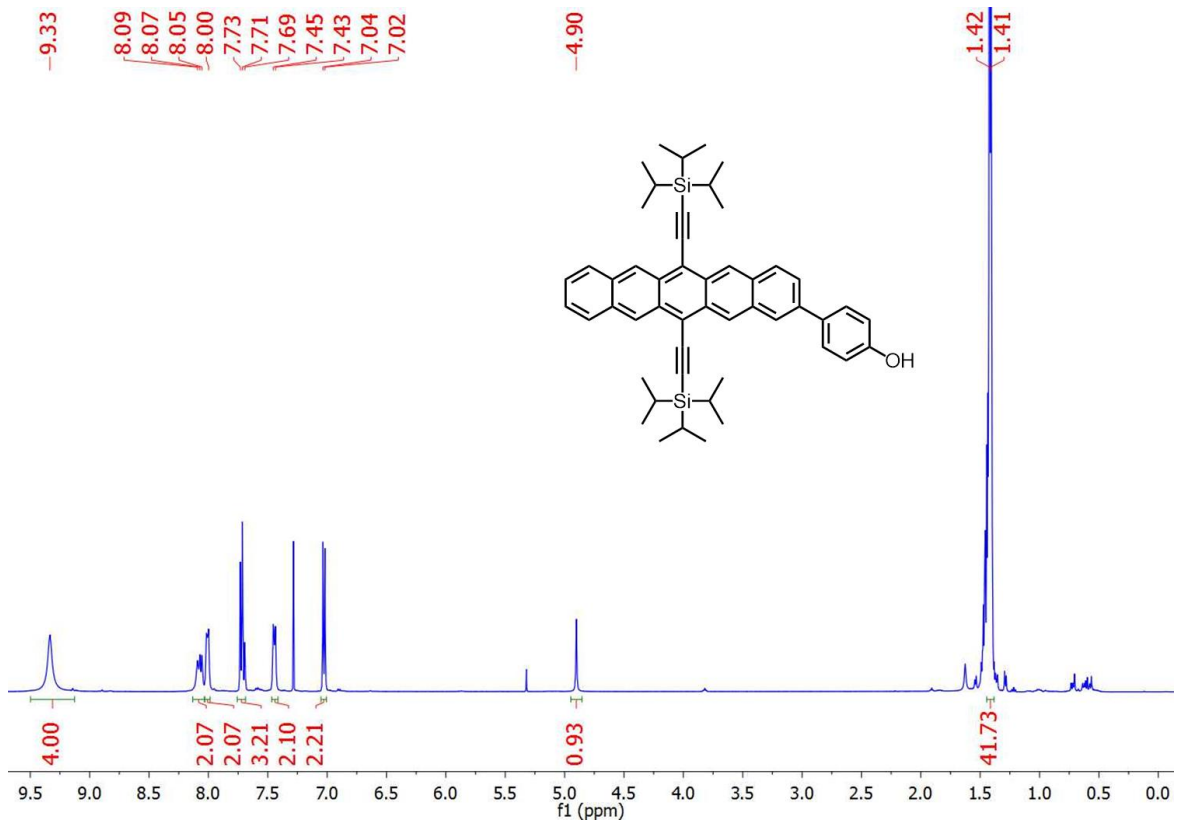
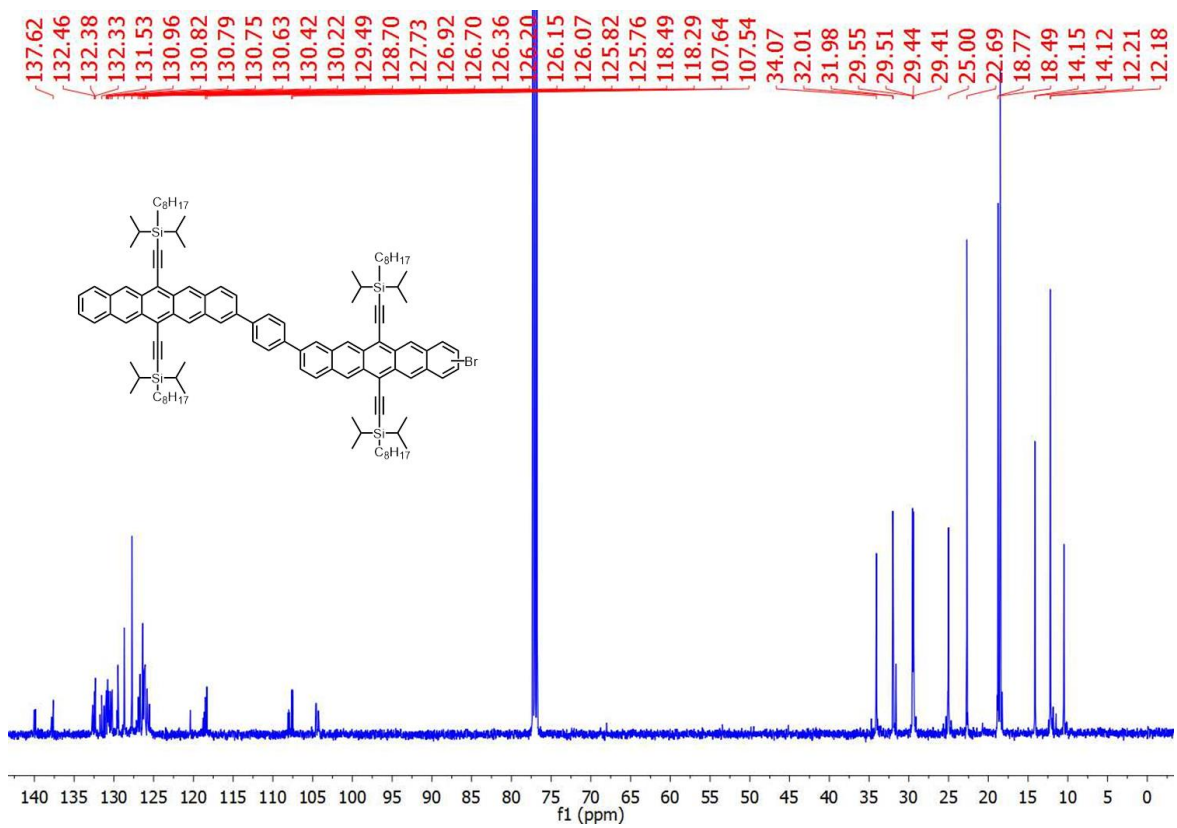
fig. S13. Normalized absorption spectra. Normalized UV-Vis spectra of BP1-Phenol (black), Iron-Oxo cluster (red), a 1:1 mixture of the two in solution (blue) and the 1:1 adduct Fe-BP1 (green).

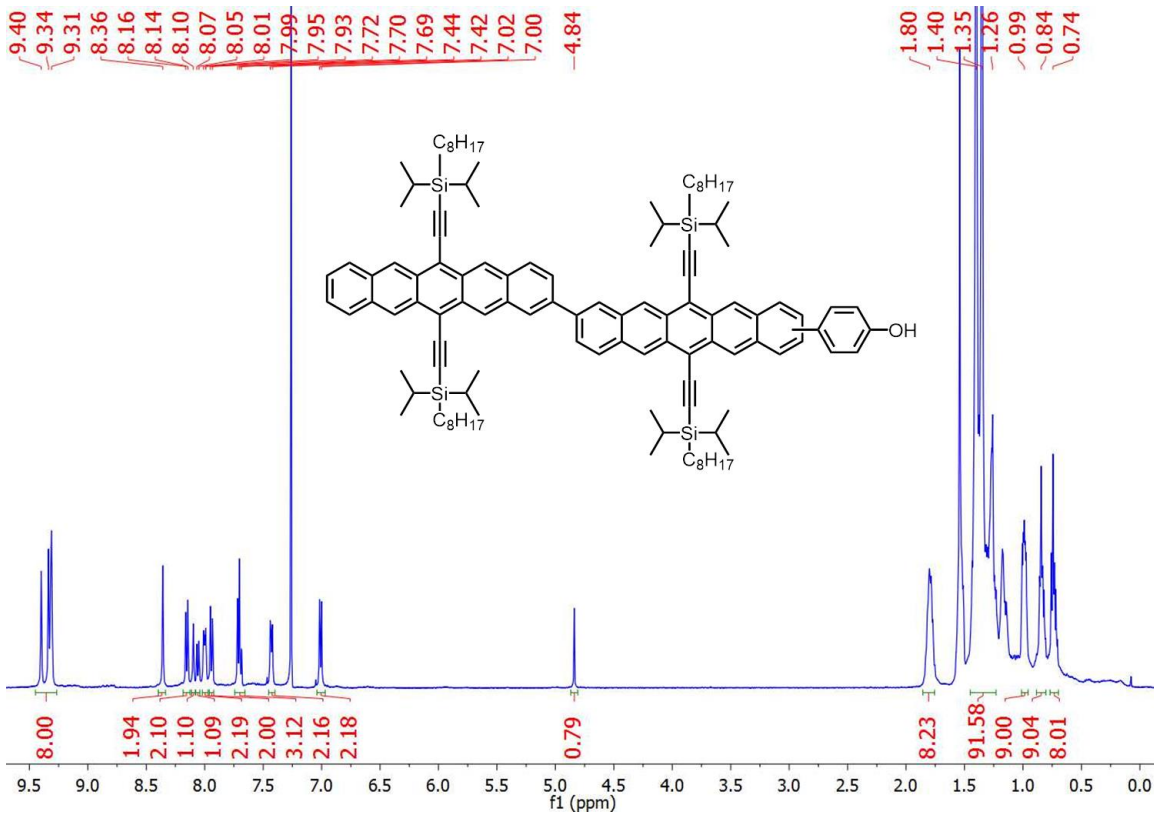
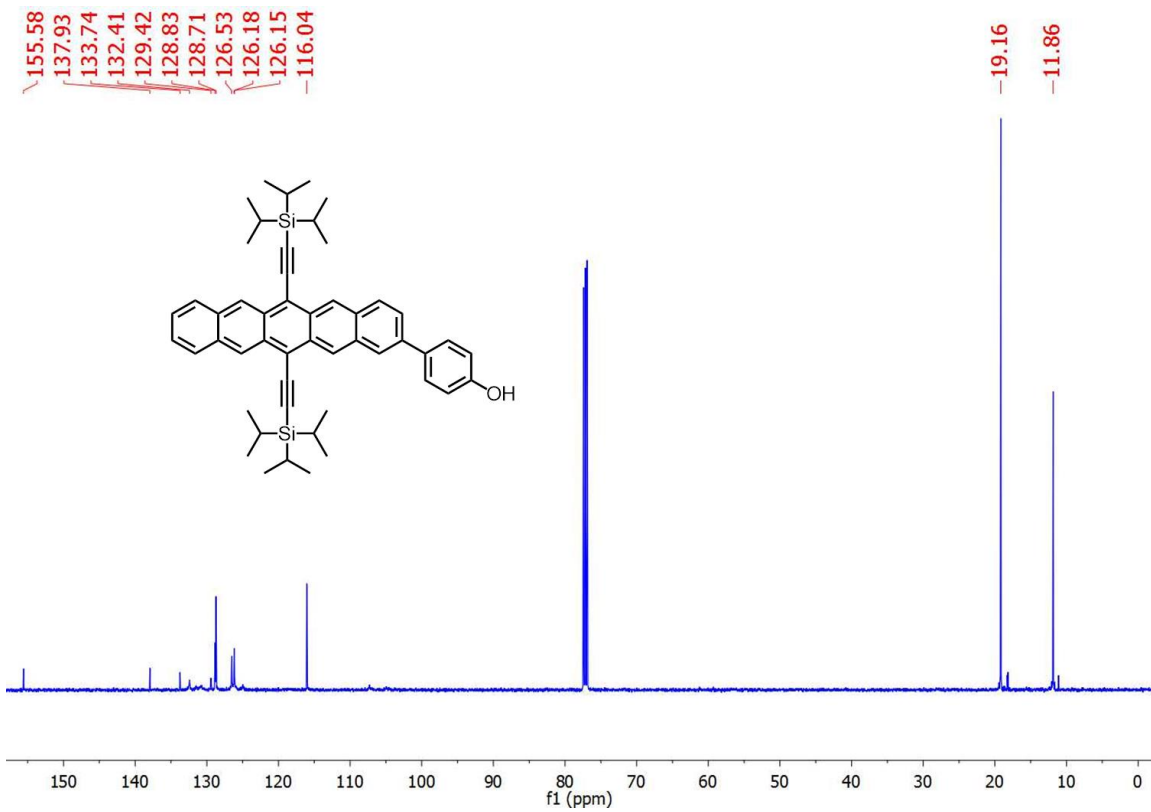
3.5. NMR Spectra

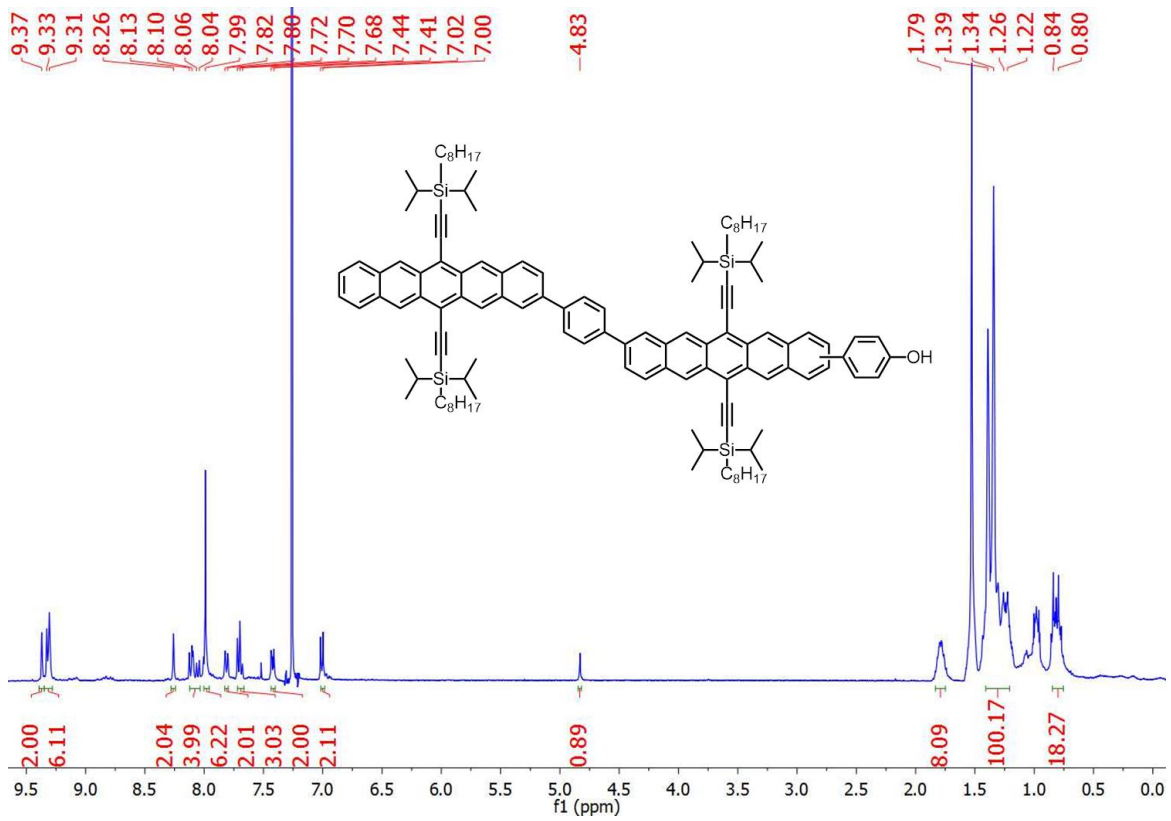
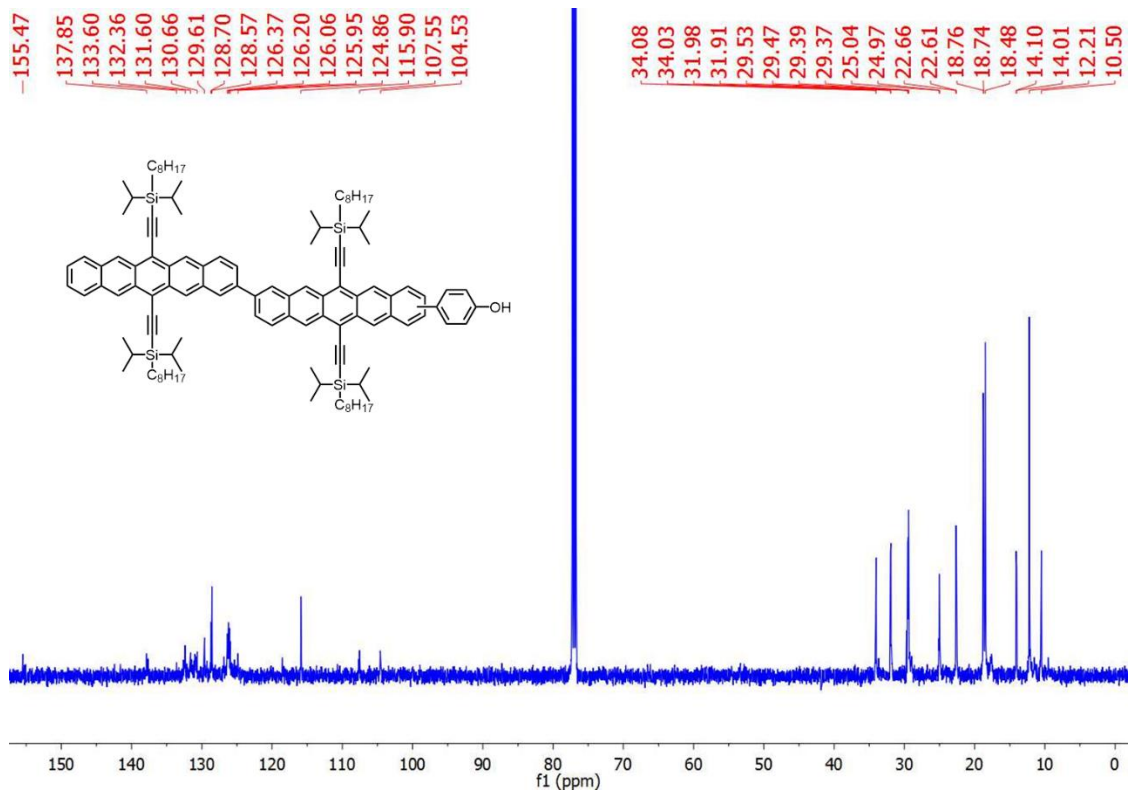
fig. S14. NMR spectrum (0–9.5 ppm), compound 2.

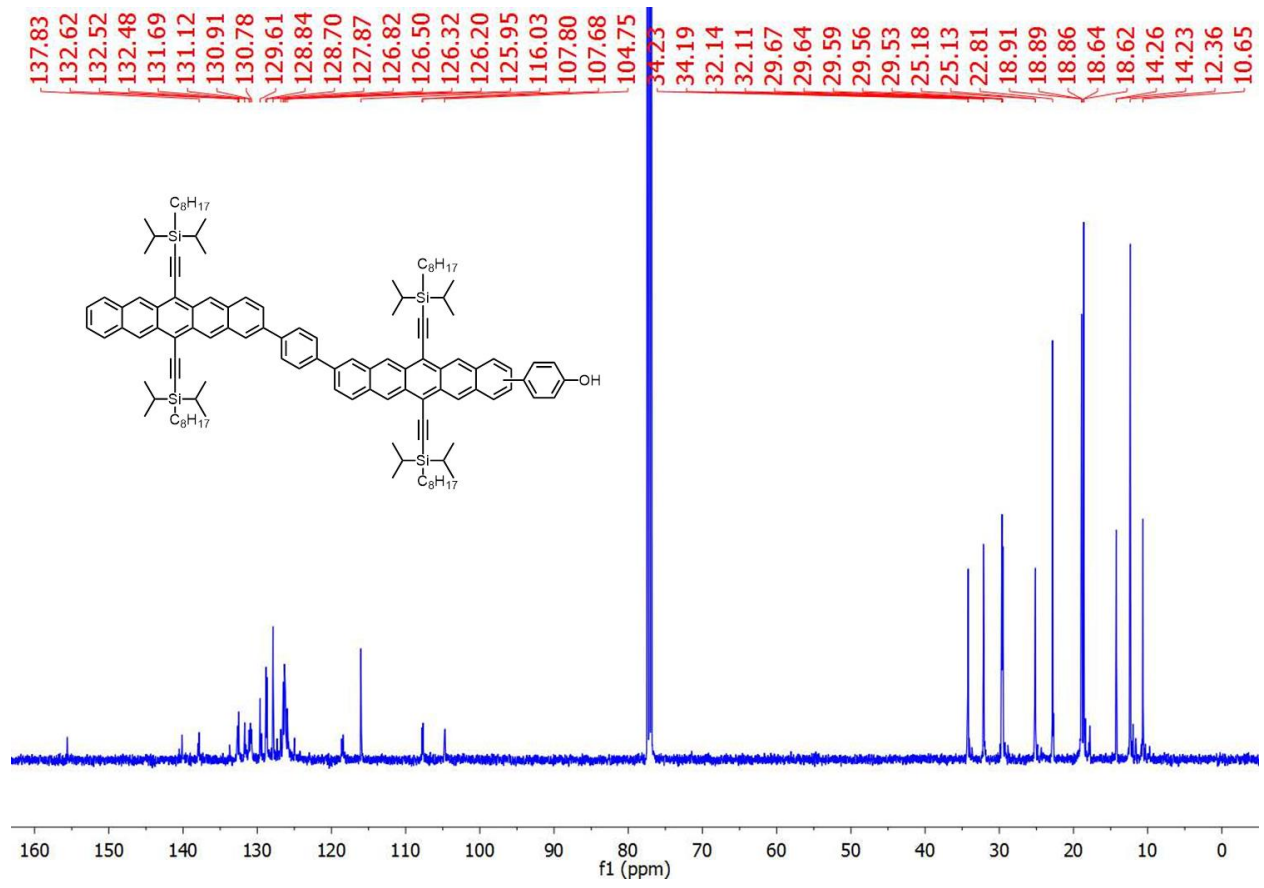




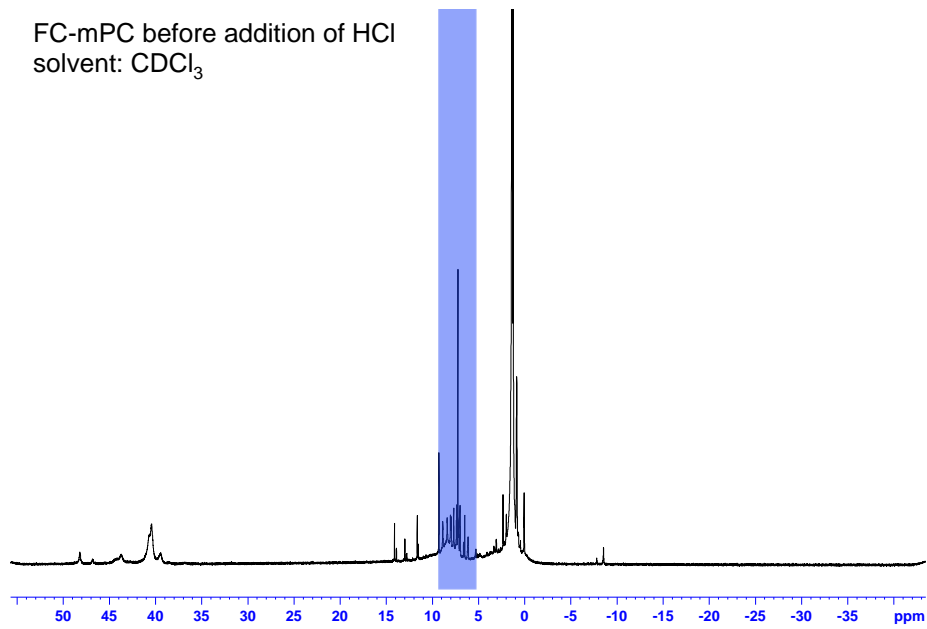








FC-mPC before addition of HCl
solvent: CDCl₃



FC-mPC after addition of HCl
solvent: CDCl₃

