A Complementary Disk-Shaped π Electron Donor-Acceptor Pair with High Binding Affinity

Liana M. Klivansky,[a] David Hanifi, [a] Gayane Koshkakaryan, [a] Daniel R. Holycross,[b] Ewa K. Gorski,[b] Qin Wu,[c] Minghui Chai[b]* and Yi Liu[a]*

[a] The Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California, USA 94720

[b] Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan, 48859

[c] Center for Functional Nanomaterasl, Brookhaven National Laboratory, Upton, NY 11973

Email: yliu@lbl.gov, chai1m@cmich.edu.

Supporting Information

Experimental Section

General methods. Reagents were purchased from Aldrich or synthesized as described. Proton and carbon nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) spectra were recorded on a Bruker Avance500 II, using the deuterated solvent as lock and tetramethylsilane as internal standard. The 2D NOESY NMR spectrum was acquired on a Varian *Inova* 500 MHz spectrometer with the residual proton signal of the solvent ($CDCl_3$) as the internal reference. All chemical shifts are quoted using the δ scale, and all coupling constants (*J*) are expressed in Hertz (Hz). High resolution electrospray mass spectra (HR ESI-MS) were measured on a VG ProSpec triple focusing mass spectrometer. Cyclic voltammetry was performed using a 273A potentiostat (Princeton Applied Research). UV-vis spectra were recorded using a Cary 5000 UV-Vis-NIR spectrometer. Grazing Incident Angle X-ray Scattering (GIAXS) was conducted using Beamline 7.3.3 at Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. TGA and DSC curves were obtained using QA5000IR and Q200 from TA Instruments, respectively. Optical and polarized optical images were taken using a Leica DM4500P microscope.

General Procedure for the Synthesis of HAT Derivatives. A mixture of trisanhydride **2** (0.44 g, 1.0 mmol), alkylamine **3a** or **3b** (0.61 g or 1.1 g, 6.0 mmol), and triethylamine (0.42 mL, 3.0 mmol) in THF (20 mL) was stirred overnight at room temperature. The solvent was evaporated, and the reaction flask was re-charged with toluene (40 ml), Ac_2O (20 mL), and TFA (0.4 mL). The mixture was heated at 80 ^oC for 3 days before it was rotavapped to give a residue, which was subjected to column chromatography (SiO_2, ethyl acetate/hexanes 1/1) to give the desired product.

HAT1. Yield: 40%. Mp. 269.5 °C (from DSC measurement). ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz): δ (ppm) 4.05 (t, J = 7.5 Hz, 6 H), 1.88-1.82 (m, 6 H), 1.47-1.29 (m, 18 H), 0.90 (t, J = 7.1 Hz, 9 H). ^{13}C NMR ($CDCl_3$, 298 K, 125 MHz): δ (ppm) 162.11, 148.79, 144.75, 39.74, 31.29, 28.40, 26.61, 22.53, 13.99. HR-MS (ESI) for $C_{36}H_{39}N_9O_6$: $[M+Na]^+$ calcd.: 716.2916, found: 716.2915 (100%).

HAT2. Yield: 66%. Mp. 190.0 °C (from DSC measurement). ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz): δ (ppm) 4.03 (t, J = 7.5 Hz, 6 H), 1.88-1.82 (m, 6 H), 1.46-1.39 (m, 12 H), 1.30-1.26 (m, 42 H), 0.87 (t, J = 6.9 Hz, 9 H). ^{13}C NMR ($CDCl_3$, 298 K, 125 MHz): δ (ppm) 162.16, 148.81, 144.91, 39.73, 31.91, 29.62, 29.61, 29.53, 29.49, 29.34, 29.13, 28.46, 26.94, 22.69, 14.13. HR-MS (ESI) for $C_{54}H_{75}N_9O_6$: $[M+Na]^+$ calcd.: 968.5746, found: 968.5741 (100%).

Computation Methods

To simplify the calculation, methyl groups were used as N-substituents on **HAT** and **TP** cores. All calculations except for the solvation of the charge transfer state were performed using Q-Chem 3.2.[s1] Geometries were fully optimized for the ground state using density functional theory[s2] with the approximate exchange-correlation functional of B3LYP[s3] plus Grimme's dispersion corrections.[s4] The same geometry was then used to calculate electronic excitations with time-dependent DFT[s5] of the same functional. A standard 6-31G** basis set and an integration quadrature with 75 radial points (Euler-Maclarin) and 302 angular points (Lebedev) were used for all calculations. The electrostatic effect of the solvation was estimated with the original COSMO model[s6] as implemented in NWChem 6.0.[s7] The dielectric constant and the solvent radius were set to be 4.8 and 3.172 angstrom, respectively. Jmol[s8] was used to plot the molecular orbitals and the electrostatic potential. The electrostatic potential was plotted on an iso-density surface with a density value of 0.01.

Table S1. The six lowest excitations from TDDFT calculation.

Excitation Energy (eV)	Strength	Orbital Transition (Amplitude)
1.5339	0.0007	HOMO->LUMO (0.9923)
1.6166	0.0002	HOMO-1 -> LUMO (0.9382) HOMO -> LUMO+1 (0.3119)
1.6532	0.0002	HOMO-1 -> LUMO+1 (0.9914)
1.6676	0.0292	HOMO-1 -> LUMO (-0.3124) HOMO -> LUMO+1 (0.9458)
1.7804	0.0002	HOMO -> LUMO+2 (0.9926)
1.8299	0.0034	HOMO-1 -> LUMO+2 (0.9888)

UV-Vis Titration.

A stock solution of an equimolar mixture of **HAT2** and **TP2** in CH_2Cl_2 (1.0 mM) was prepared. Solutions with desired concentration were obtained by adding an aliquot of CH_2Cl_2 to separate containers with 1.0 mL of above stock solution. The corresponding UV-vis spectra were recorded. The absorptions (*A*) of the charge-transfer (CT) band at λ = 574 nm at different concentrations are listed in Table S1.

Table S1. List of absorptions of the CT band at different concentrations of **HAT2/TP2**.

c_0/mM	1.0	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10
A	2.65	2.46	2.13	1.84	1.55	1.27	0.934	0.684	0.419	0.173

For the equilibrium:

$$\mathbf{HAT2} + \mathbf{TP2} \rightleftharpoons \mathbf{Complex} \qquad K_\mathrm{a}$$

$K_\mathrm{a} = c_\mathrm{complex}/(\, c_\mathrm{HAT2}\, c_\mathrm{TP2})$

$c_\mathrm{HAT2} = c_0 - c_\mathrm{complex}$ (c_0 is the initial concentration of **HAT2** and **TP2**)

Since c_HAT2 is kept the same as c_TP2, thus $K_\mathrm{a} = c_\mathrm{complex} /(c_0 - c_\mathrm{complex})^2$

According to Beer's Law, $A = \varepsilon \mathrm{b} c_\mathrm{complex}$, ($\varepsilon$ is the molar extinction coefficient, b is the light path length). Substituting all c_complex with $A/\varepsilon\mathrm{b}$, the following equation is obtained.

$K_\mathrm{a} = \varepsilon\mathrm{b}A/(c_0\varepsilon\mathrm{b}\text{-}A)^2$, which transforms to the following:

$$K_a A^2 - (2c_0\varepsilon b K_a + \varepsilon b)A + K_a \varepsilon^2 b^2 c_0{}^2 = 0$$

By solving this equation and using b = 1 cm, the following function is obtained:

$$A = \varepsilon \frac{(2c_0K_a + 1) \pm \sqrt{4c_0K_a + 1}}{2K_a}$$

From the non-linear curve fitting using Origin 8.5,[S9] K_a is determined to be 2.6(±0.8) $\times 10^4$ M^{-1} and the extinction coefficient is 3.3(±0.1)$\times 10^3$ M^{-1} cm^{-1}, with an adjusted R-square of 0.9986.

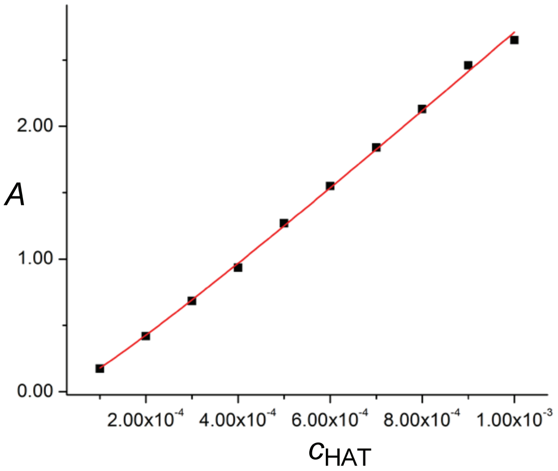

Figure S1. The plot from the non-linear curve fitting.

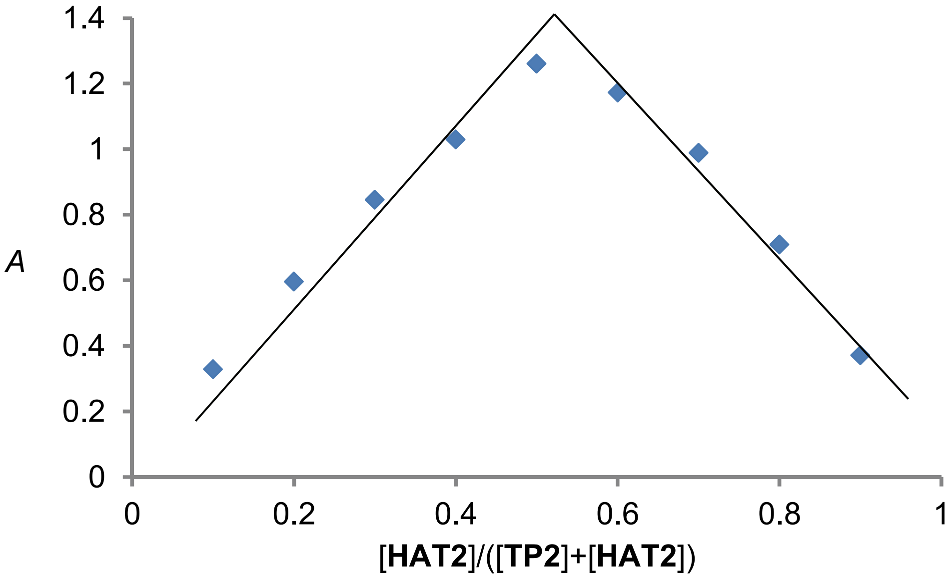

Figure S2. Job plot showing the 1:1 stoichiometry of the **HAT2/TP2** complex. The absorption maximum of the charge transfer band is plotted against the molar ratio of **HAT2** in the total DA mixture. The total DA concentration of **HAT2** and **TP2** was kept at 0.5 mM.

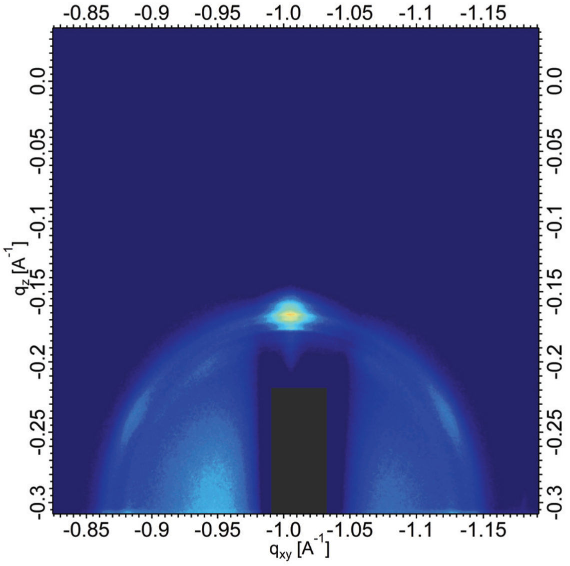

Figure S3. GIWAXS of **HAT1/TP1** 1:1 mixture.

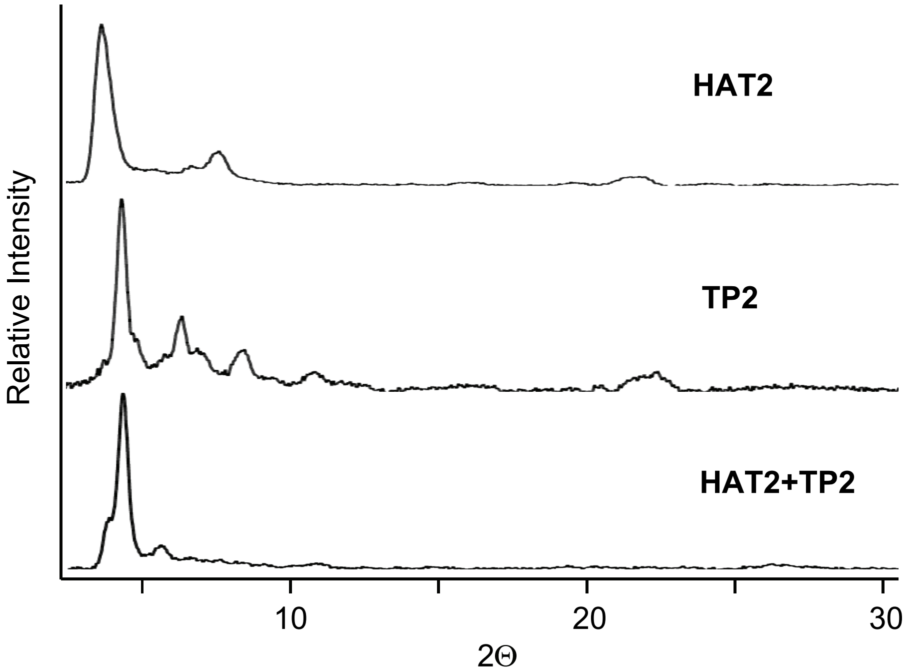

Figure S4. Stacked Powder XRD Spectra of **TP2**, **HAT2** and **TP2/HAT2** (1:1).

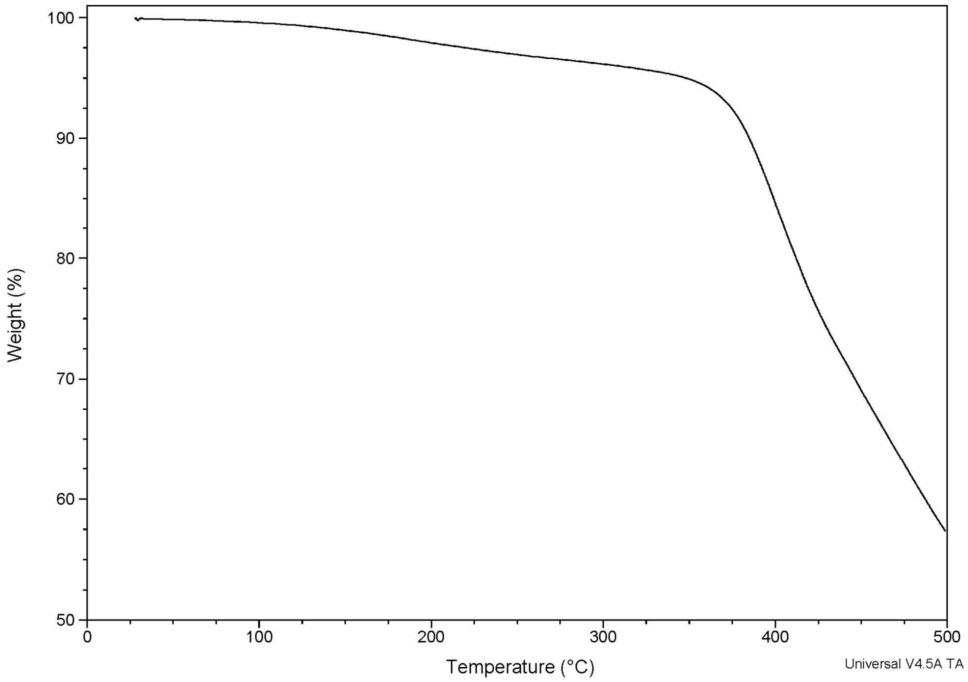

Figure S5. TGA curve of **HAT1**.

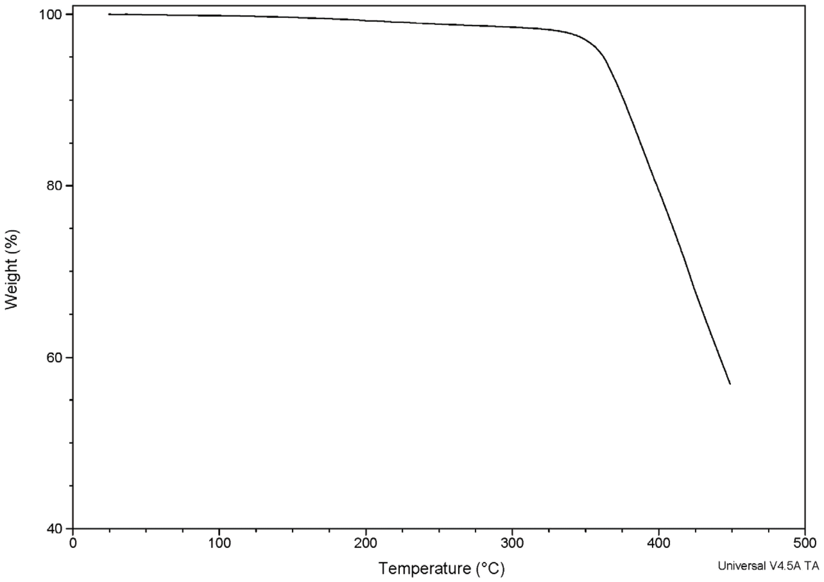

Figure S6. TGA curve of **HAT2**.

NMR Analyses of HAT2/TP2.

All NMR experiments on **HAT2**, **TP2** and 1:1 **HAT2/TP2** complex were performed on a Varian *Inova* 500 MHz spectrometer using a $^{1}H/X$ (X is tunable from ^{15}N to ^{31}P) ultra linear gradient probe. 1D ^{1}H NMR spectra were acquired with 4.8 kHz spectral window, 1.5 s acquisition delay, 1s relaxation delay, 5.75 µs (about 45°) pulse width and 128 scans. 2D gradient enhanced ^{1}H-^{1}H COSY NMR spectra were collected with 4.8 kHz spectral window, 0.512 s acquisition delay, 1s relaxation delay, 9.0 µs ^{1}H 90° pulse width and 8 scans averaged for 1024 t_1 increments. All NMR data were processed using Varian 6.1C VNMR software on a SUN Blade 2000 workstation.

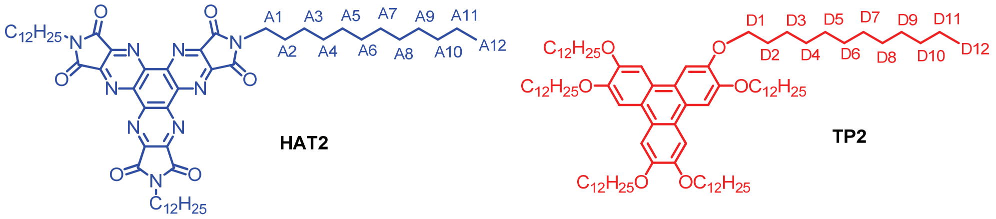

Figure S7. The structures of **HAT2** & **TP2** with numerical labels for the aliphatic chains.

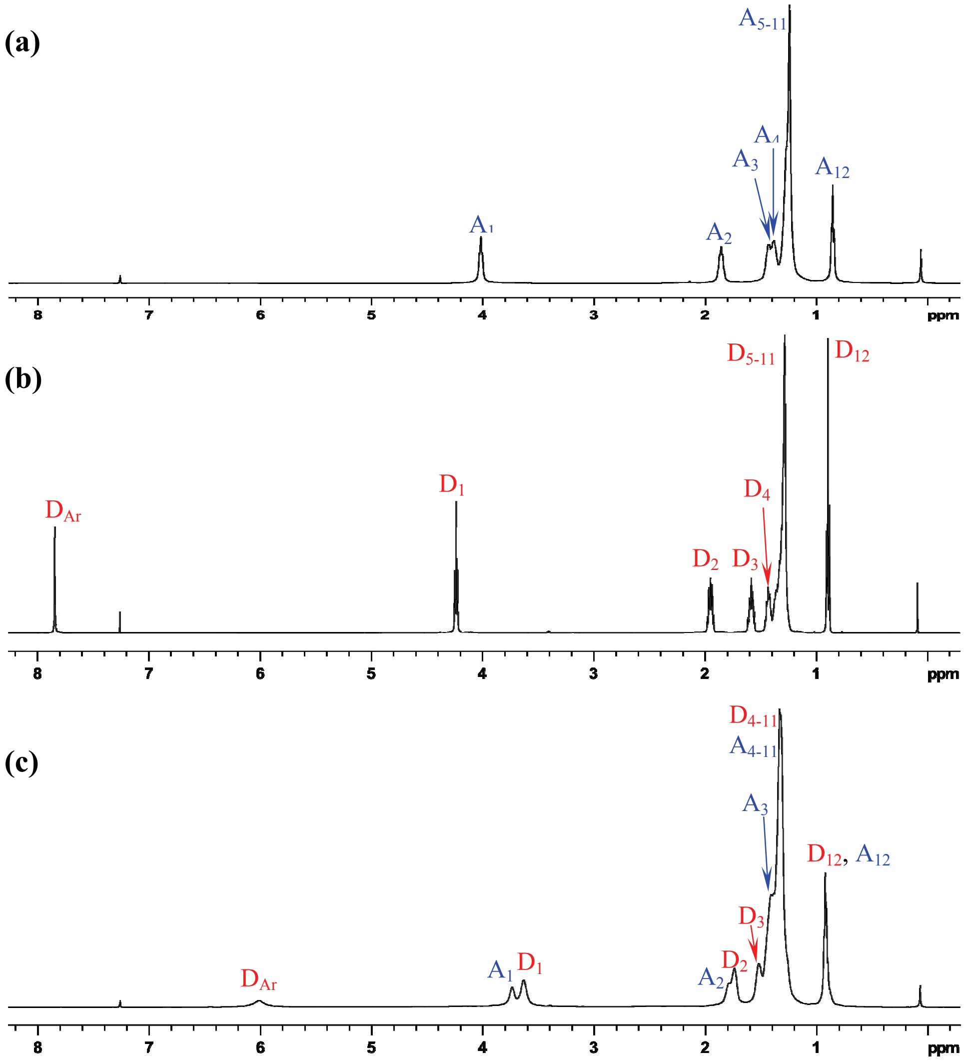

Figure S8. 1D ^{1}H NMR spectra of (a) **HAT2** (acceptor), (b) **TP2** (donor) and (c) 1:1 **AT2/TP2** complex (40 mM) in $CDCl_3$ with peak assignments based on the labels in Figure S2.

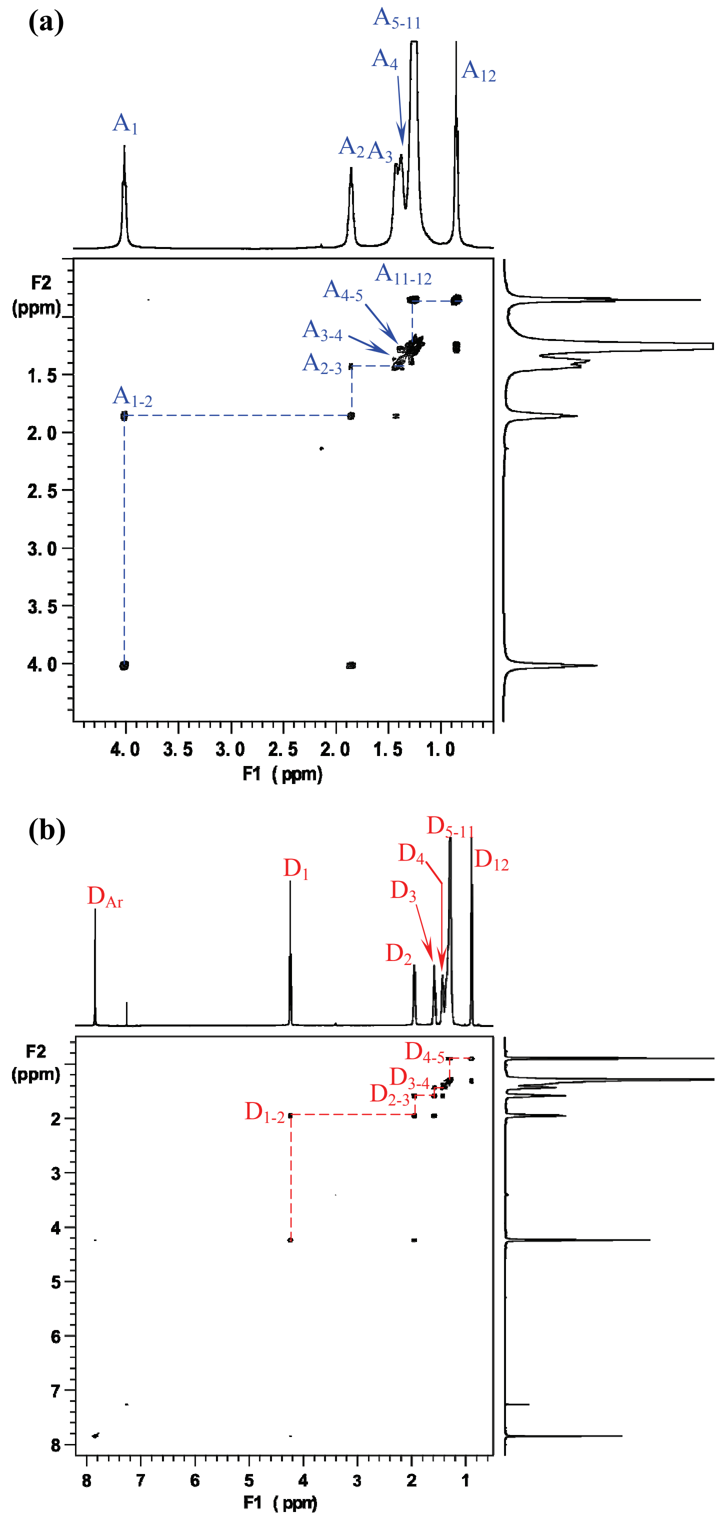

Figure S9. Vicinal ^{1}H-^{1}H (i.e. 3-bond) correlation 2D COSY NMR spectra of (a) **HAT2** and (b) **TP2** in $CDCl_3$ with peak assignments based on the labels in Figure S2.

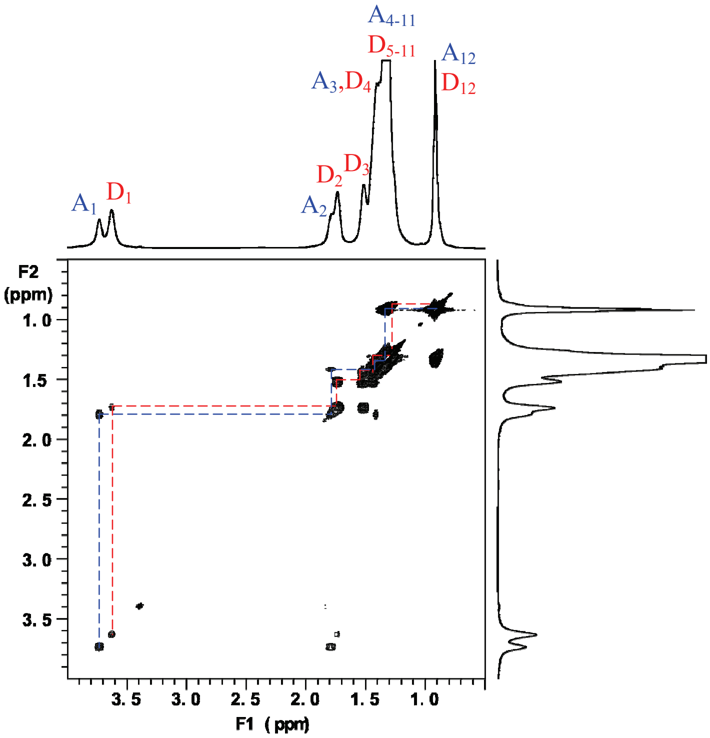

Figure S10. Vicinal ^1H-^1H (i.e. 3-bond) correlation 2D COSY NMR spectrum of 1:1 **HAT2/TP2** mixture in $CDCl_3$ with peak assignments based on the labels in Figure S2.

.

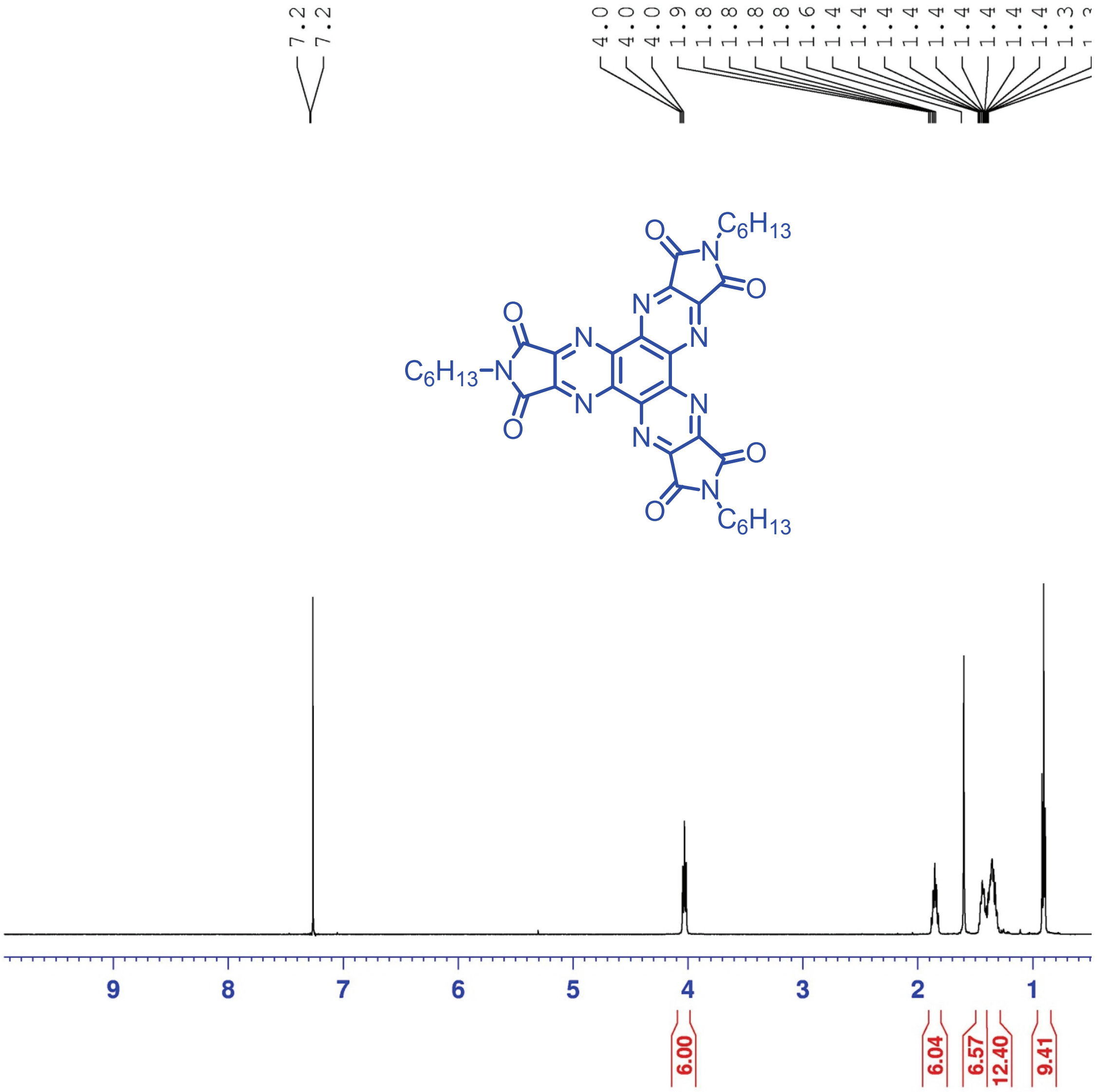

Figure S11: ^{1}H NMR spectrum of **HAT1** ($CDCl_3$, 298 K, 500 MHz).

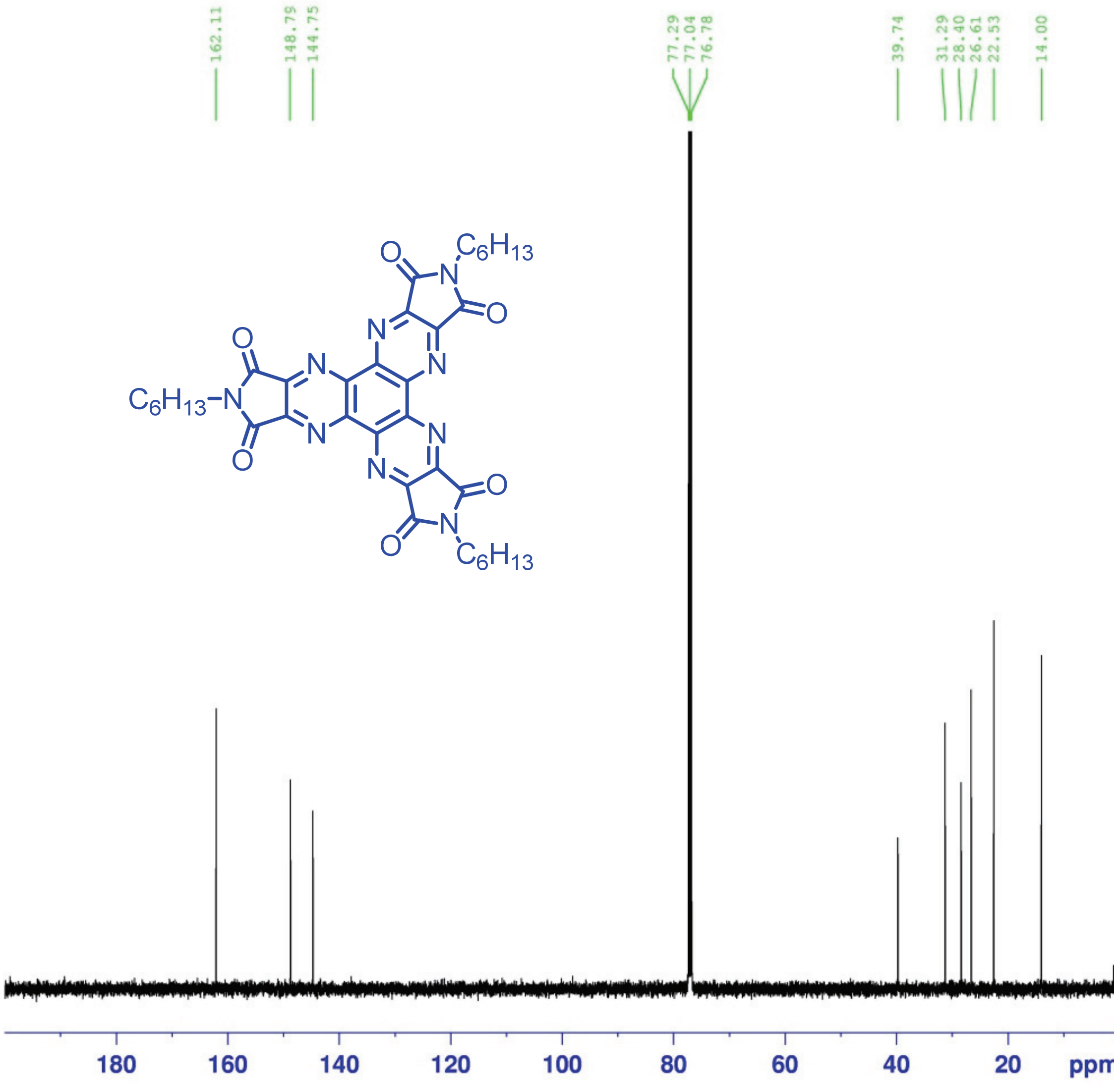

Figure S12: ^{13}C NMR spectrum of **HAT1** ($CDCl_3$, 298 K, 125 MHz).

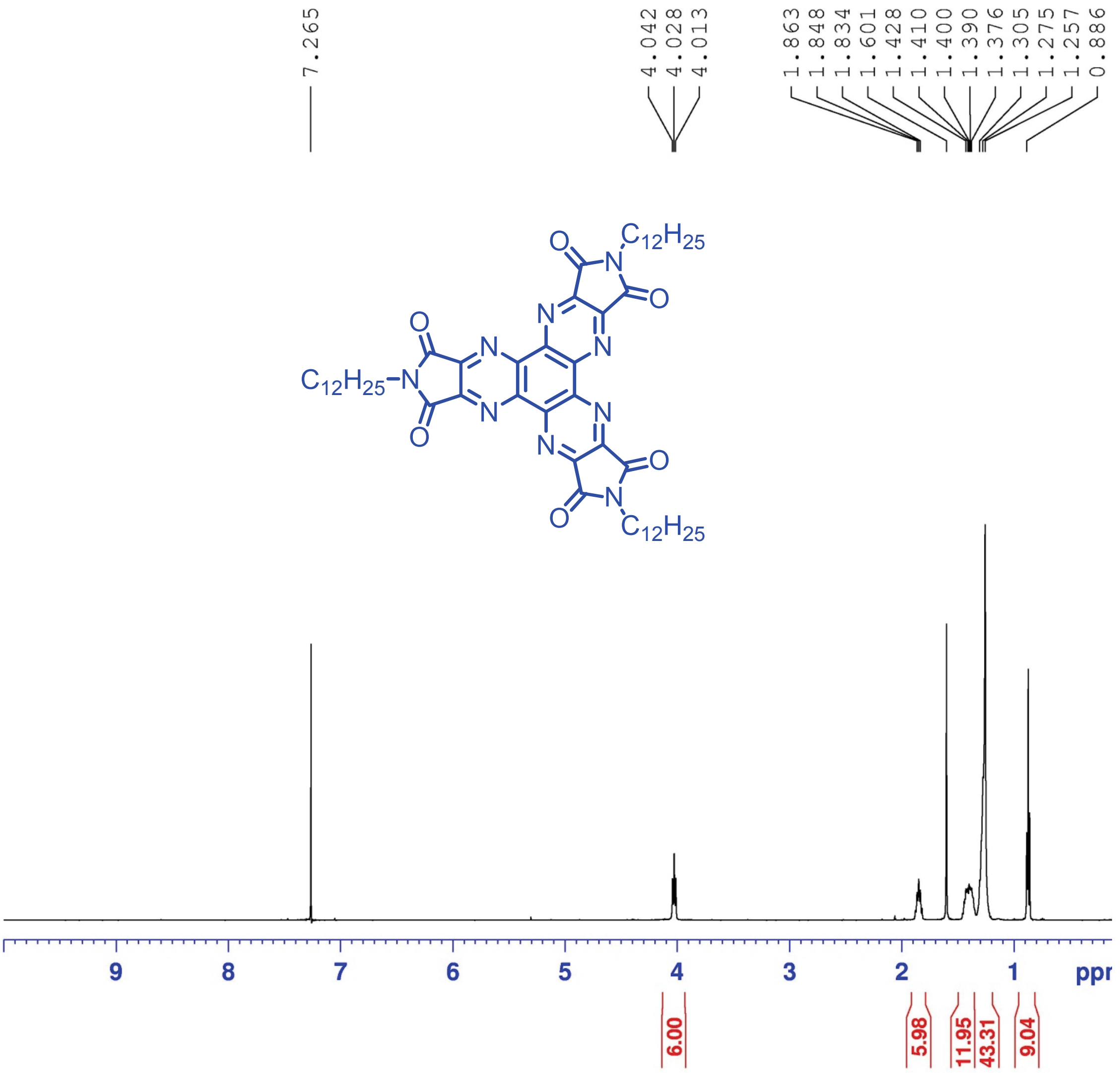

Figure S13: ^{1}H NMR spectrum of **HAT2** ($CDCl_3$, 298 K, 500 MHz).

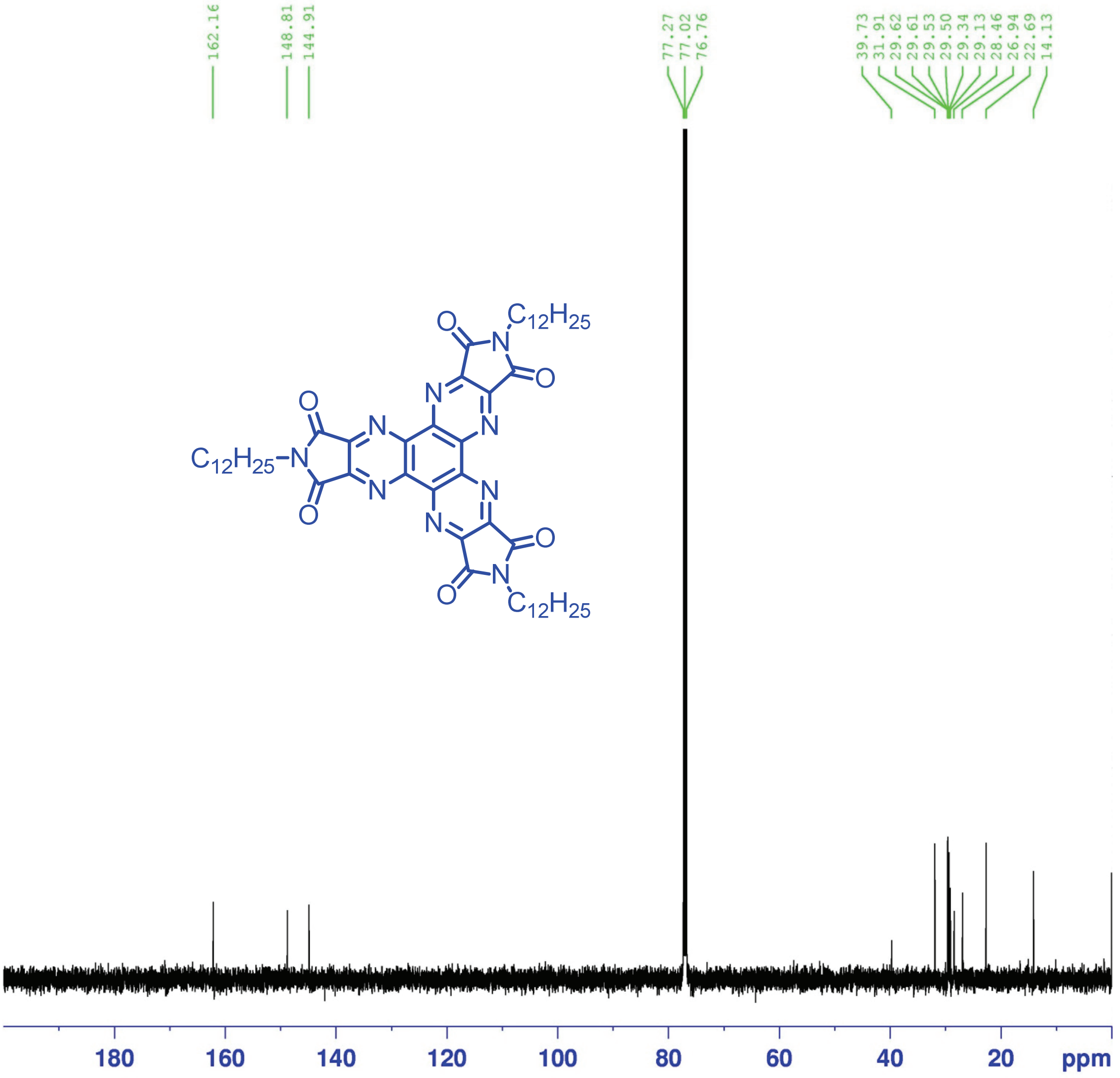

Figure S14: ^{13}C NMR spectrum of **HAT2** ($CDCl_3$, 298 K, 125 MHz).

References:

S1. Q-Chem is a product of Q-Chem. Inc.

S2. (a) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864. (b) Kohn,W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

S3. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C. T., Yang, W. T. & Parr, R. G. *Phys. Rev. B* **1988,** *37*, 785–789.

S4. Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.

S5. (a) Runge; E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997-1000. (b) Casida, M. E. in "Recent Advances in Density Functional Methods", Part I, edited by Chong, D. P., World Scientific: Singapore, 1995.

S6. Klamt, A.; Schüürmann, G. *J.Chem.Soc.Perkin Trans*. **1993**, *2*, 799.

S7. Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; de Jong W. A., *Comput. Phys. Commun*. **2010**, *181*, 1477.

S8. Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/

S9. Origin 8.5 is a data analysis and graphing software from OriginLab, US.