Electronic Supplementary Material (ESI) for Faraday Discussions.

"Energy Transfer within Self-Assembled Cyclic Multichromophoric Arrays Based on Orthogonally Arranged *Donor* - *Acceptor* Building Blocks"

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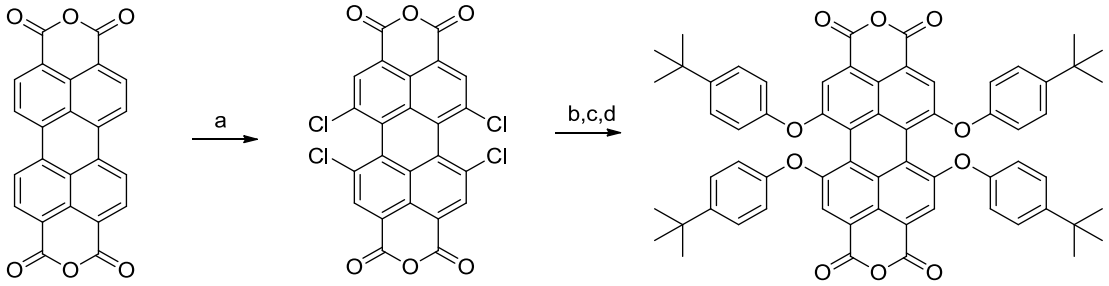
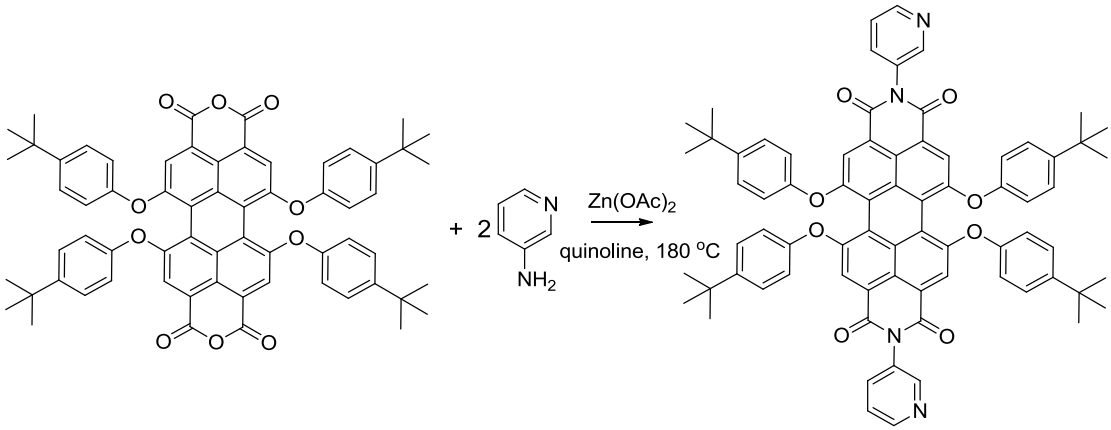
Synthesis of 1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid.



Starting material 1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisanhydride was prepared from perylene-3,4,9,10-tetracarboxylic dianhydride according to literature procedures: a) chlorosulfonic acid, iodine, 70 °C, 24 h, (ref. 1), b) n-butylamine, PrOH/H_2O, 70 °C, 10 h, c) 4-(tert-butyl)phenol, K_2CO_3, 1-methyl-2-pyrrolidinone, 130 °C, 16 h, Ar,. d) KOH, H_2O, t-BuOH, reflux, 16 h, (ref. 2).

Synthesis of (*N,N'-Di(3-pyridyl)-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide*), compound 3.



Procedure according to reference 3. 1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisanhydride (103 mg, 0.10 mmol), 3-aminopyridine (48 mg, 0.51 mmol) and zinc(II)acetate (61 mg, 0.33 mmol) were allowed to react in 3 ml of quinoline, at 180 °C, under argon atmosphere. After stirring for 3 h the reaction mixture was cooled to room temperature and 25 ml of HCl 2 N were added. The precipitate was collected, filtered, washed twice with 20 ml of water, 2x10 ml MeOH and dried. Purification by silica gel column chromatography with eluent CH_2Cl_2/MeOH 98:2 gave 85 mg of product (71% yield). mp>290 °C; ^{1}H NMR ($CDCl_3$): δ 8.68 (d, J=4.12 Hz, 2H), δ 8.56 (s, 2H), δ 8.27 (s, 4H), δ 7.64 (d, J=7.79 Hz, 2H), δ 7.46 (m, 2H), δ 7.25 (d, J=7.79 Hz, 8H), δ 6,87 (d, J=7.79 Hz, 8H), δ 1.28 (s, 36H); ^{13}C NMR ($CDCl_3$): 163.42, 156.26, 152.78, 149.83, 149.67, 147.69, 136.54, 133.28, 132.03, 126.85, 123.87, 122.26, 121.03, 120.29, 119.82, 119.44, 34.52, 31.57; Anal. Calcd for $C_{74}H_{64}N_4O_8$: C, 78.15; H, 5.67; N, 4.93. Found: C, 77.85; H, 5.69; N, 4.92.

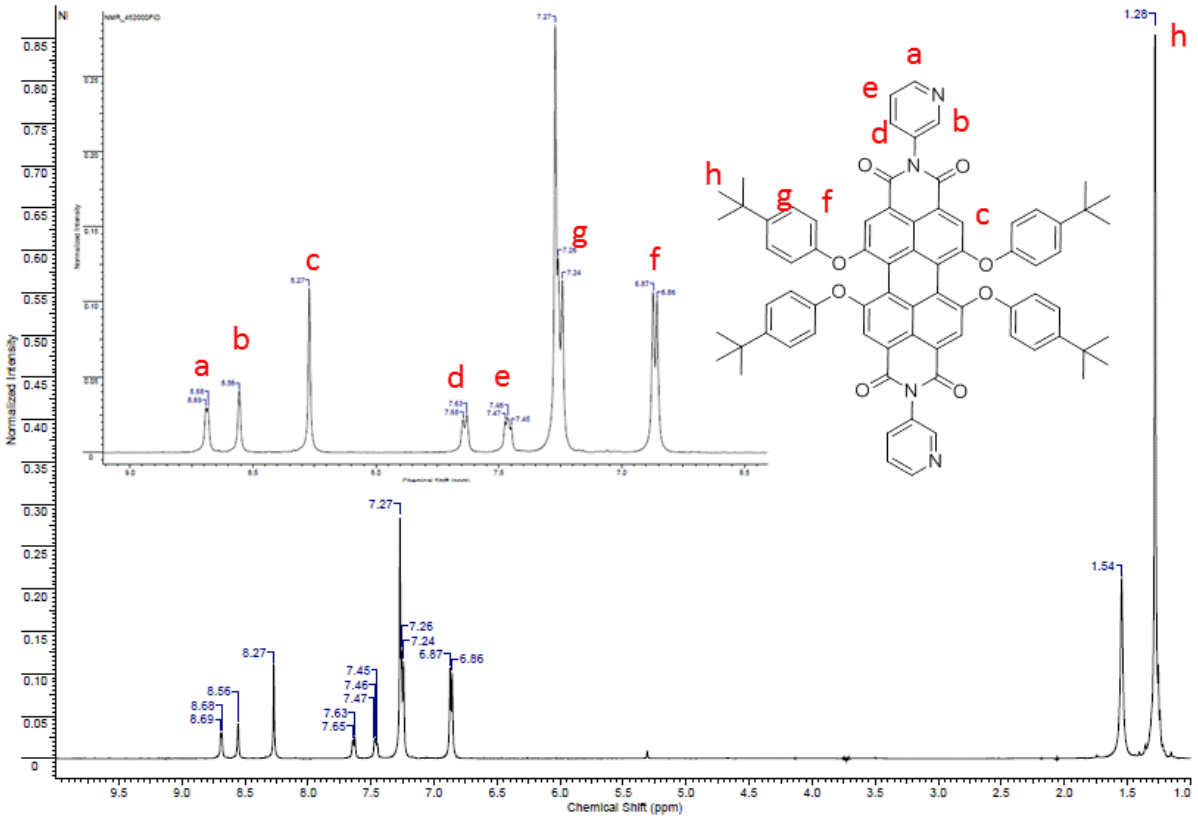


Figure S1. ^{1}H NMR (500 MHz) spectrum of **3** in $CDCl_3$.

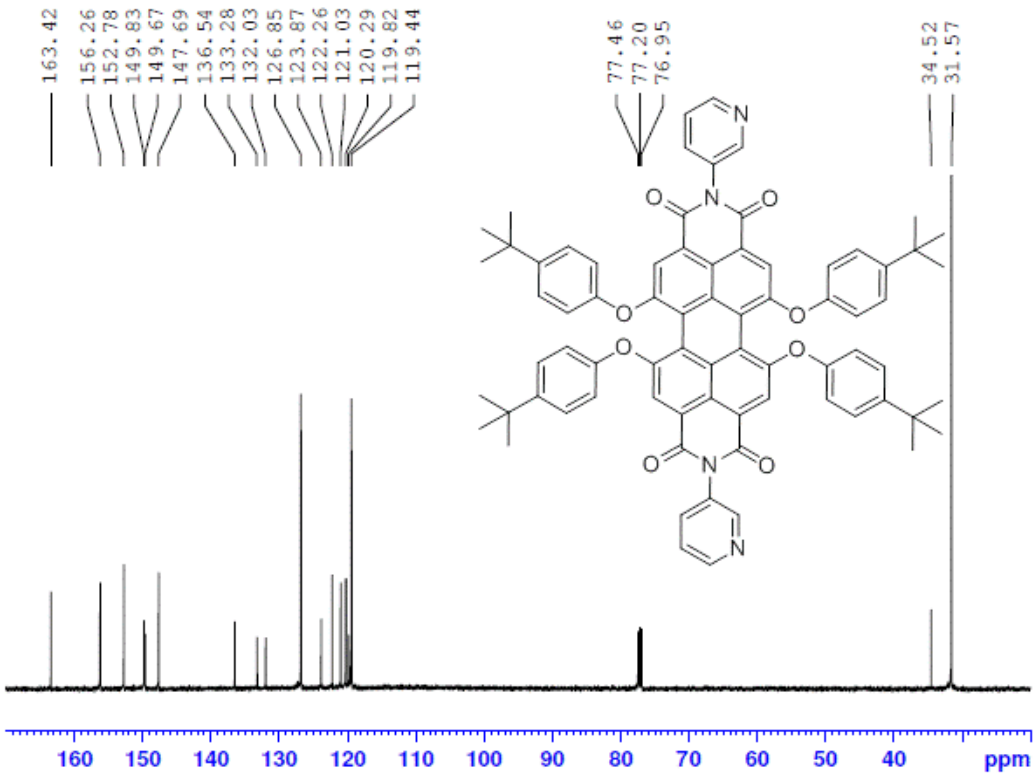
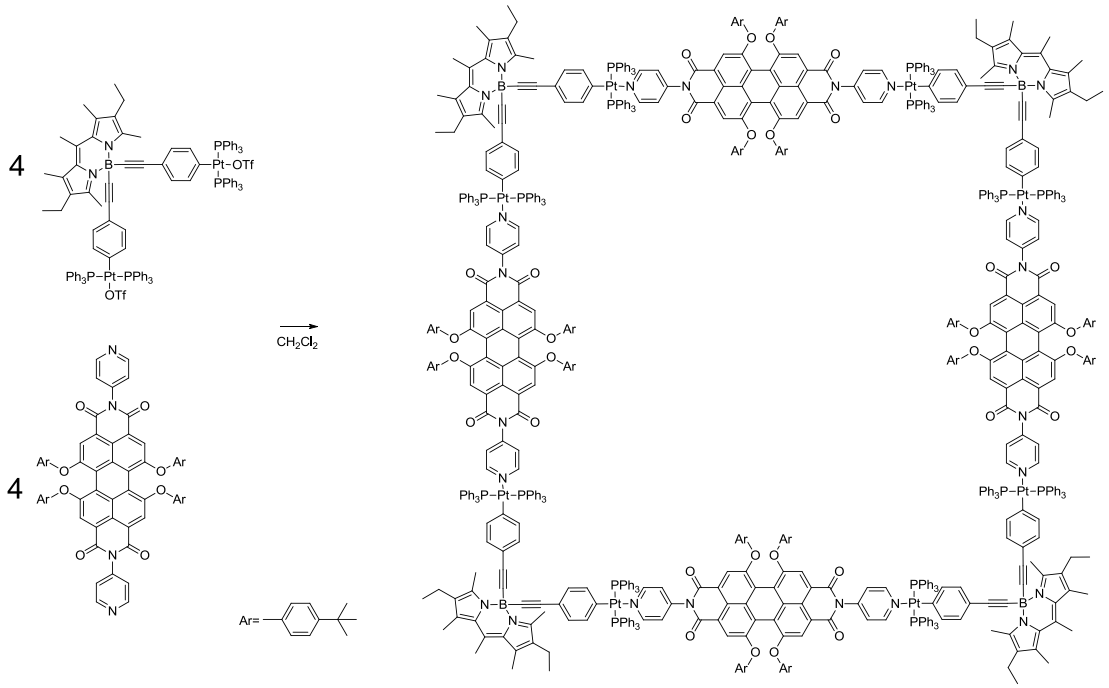


Figure S2. ^{13}C NMR (125 MHz) spectrum of **3** in $CDCl_3$.

Self-assembly of [4+4] structure 4



A solution of 20.0 mg (0.0090 mmol) of Bodipy in 2 ml of CH_2Cl_2 was added to 10.1 mg (0.089 mmol) of perylene **2** in 4 ml of CH_2Cl_2 in a 20 ml vial under continuous stirring at rt for 1 hour. The volume was reduced to half under a gentle stream of nitrogen. The product precipitated by diffusion of diethyl ether over 24 hours, was washed with 2x4 ml of ethyl acetate and dried. Yield 71.8 % (21.6 mg). ^{1}H NMR ($CDCl_3$): δ 8.18 (s, 32H), δ 7.33 (s), δ 6.82 (d, J=8.6 Hz, 32H), δ 6.73 (d, J=5.4, 16H), δ 6.60 (d, J=7.8, 16H), δ 6.34 (d, J=7.4, 16H),δ 2.69 (s, 24H), δ 2.60 (s, 12H), δ 2.44 (s, 16H), δ 2.33 (s, 24H), δ 1.28 (s, 144H), δ 1.06 (s, 24H); ^{31}P {^{1}H} NMR ($CDCl_3$, 121.4 MHz) δ 20.73 ppm (s, ^{195}Pt satellites, $^1J_{Pt-P}$=2994 Hz)); ESI-MS m/z 1768.1987 $[M\text{-}7OTf]^{7+}$.

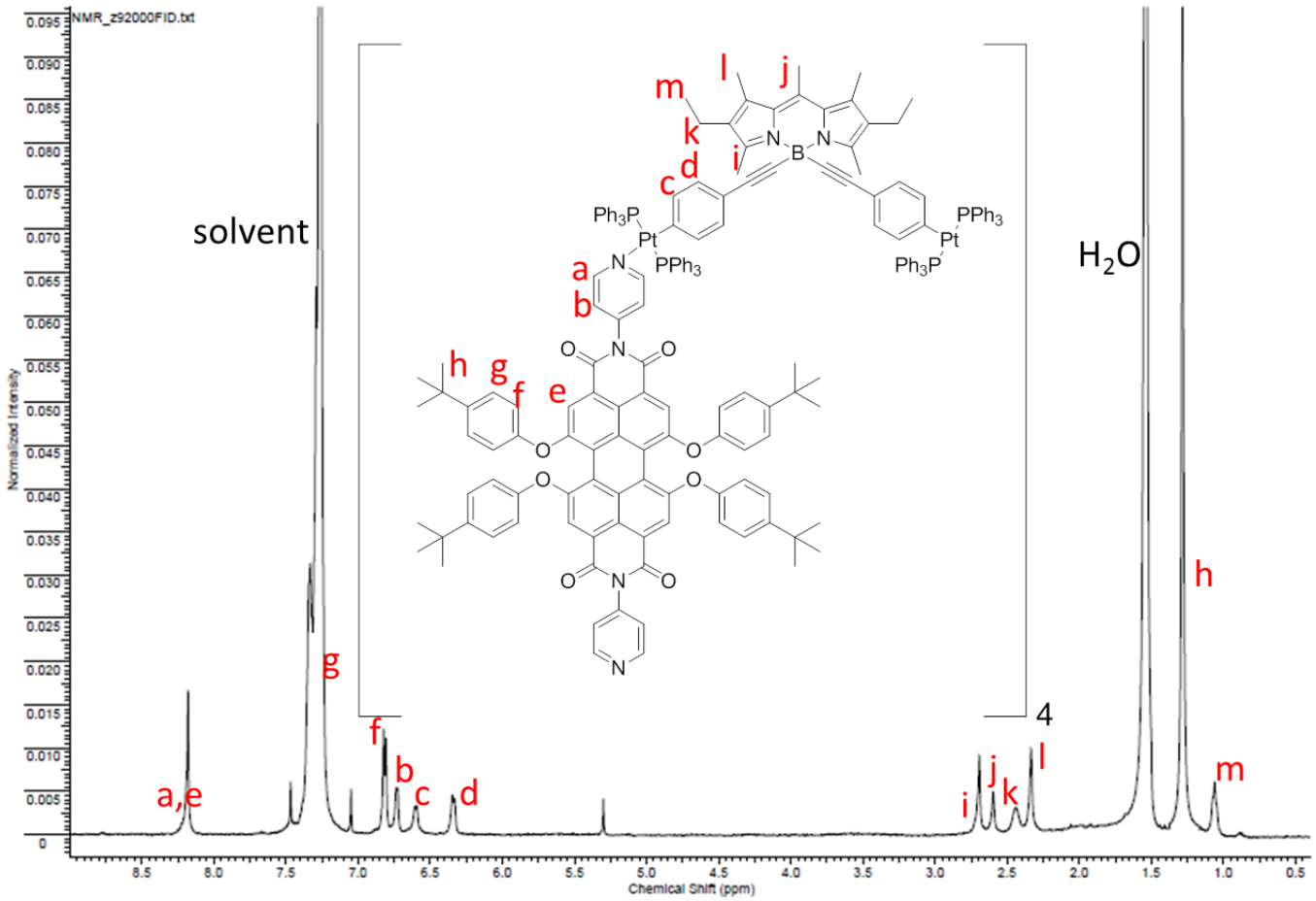
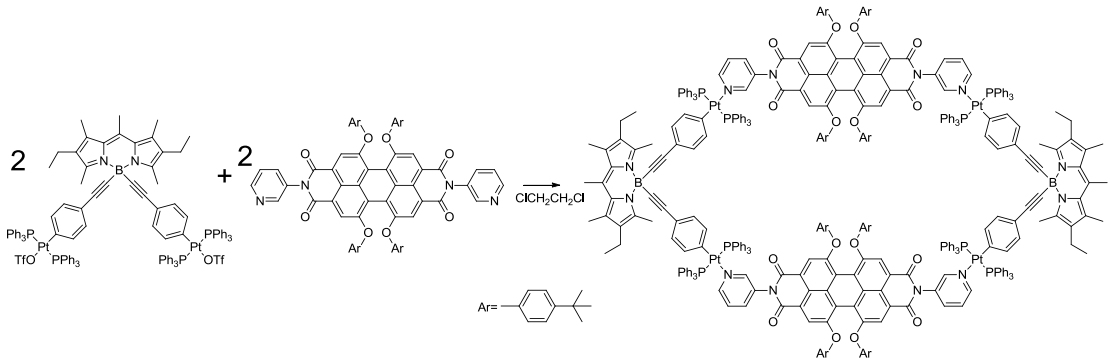


Figure S3. ^{1}H NMR (500 MHz) spectrum of **4** in $CDCl_3$.

Self-assembly of [2+2] structure 5



A solution of 20.4 mg (0.0092 mmol) of Bodipy in 2 ml of $ClCH_2CH_2Cl$ was added to 10.3 mg (0.091 mmol) of perylene **3** in 4 ml of $ClCH_2CH_2Cl$ in a 20 ml vial under continuous stirring at rt for 1 hour. The volume was reduced to half under a gentle stream of nitrogen. The product precipitated by diffusion of diisopropyl ether over 72 hours, was washed with 2x4 ml of ethyl acetate and dried. Yield 75.0 % (23.1 mg). ^{1}H NMR ($CDCl_3$): δ 8.30 (s, 4H), δ 8.16 (s, 8H), δ 7.72 (d, J=5.1 Hz, 4H), δ 7.32, δ 6.93 (d, J=8.6 Hz, 16H), δ 6.66 (m, 12H), 6.37 (br, 8H), δ 2.71 (s, 12H), δ 2.61 (s, 6H), δ 2.44 (m, 8H), δ 2.34 (m, 12H), δ 1.32 (s, 72H), (δ 1.07 (t, J=7.3 Hz, 12H); ^{31}P {^{1}H} NMR ($CDCl_3$, 121.4 MHz) δ 20.75 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$=3140 Hz); ESI-MS m/z 2087.669 $[M-3OTf]^{3+}$,m/z 1528.512 $[M-3OTf]^{3+}$.

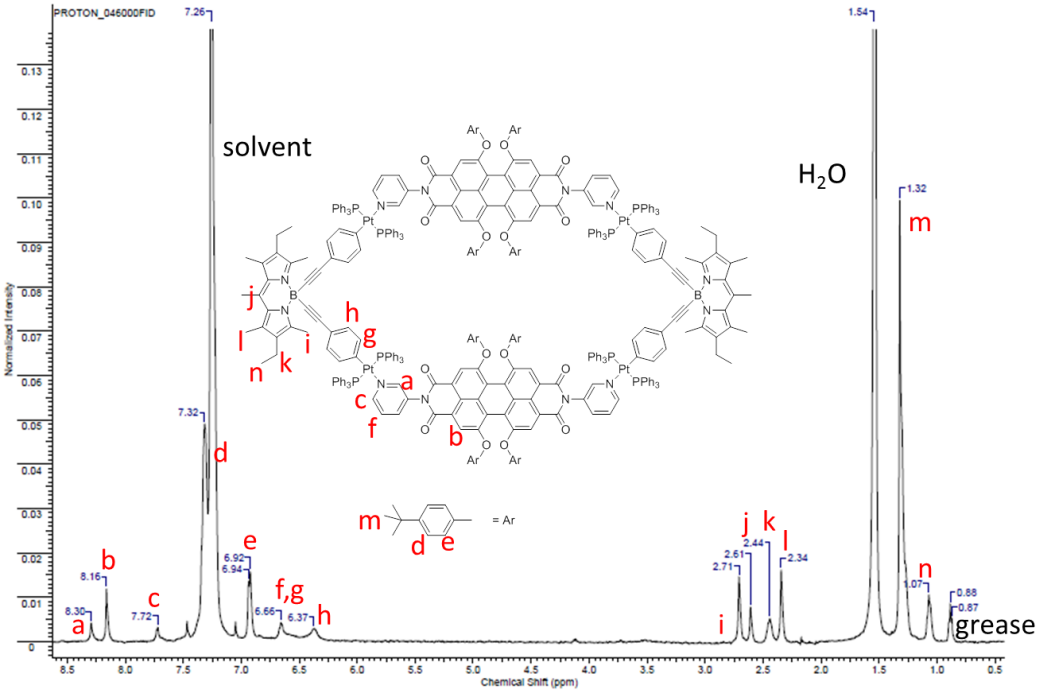


Figure S4. ^{1}H NMR (500 MHz) spectrum of **5** in $CDCl_3$.

High-resolution electrospray ionization mass spectrometry (ESI –MS)

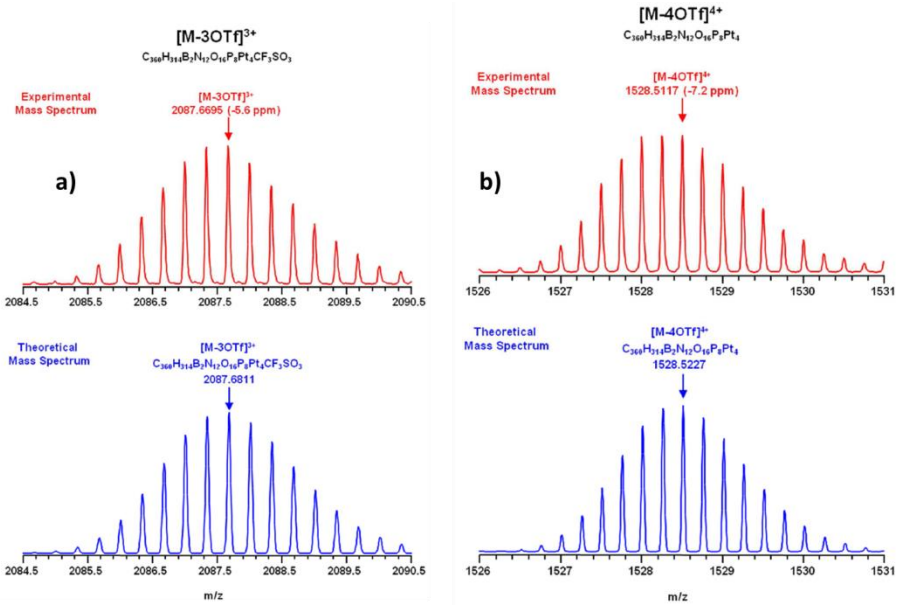


Figure S5. Experimental (red) and theoretical (blue) ESI mass spectra of a) $[M\text{-}3OTf]^{3+}$ and b) $[M\text{-}4OTf]^{4+}$ for assembly **5.**

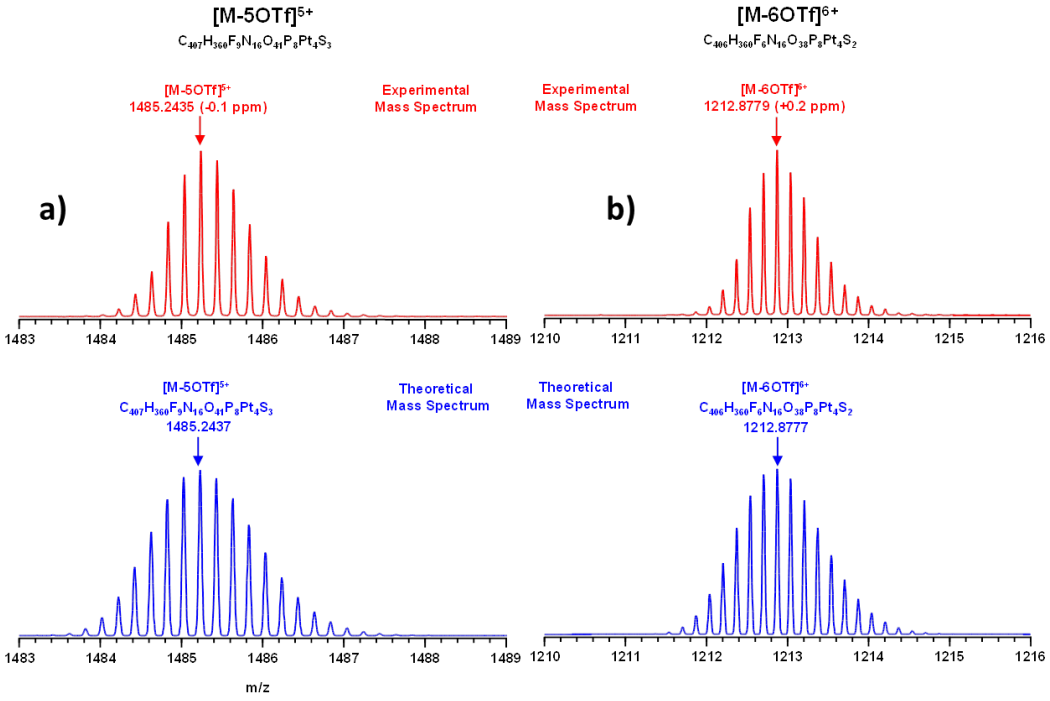


Figure S6. Experimental (red) and theoretical (blue) ESI mass spectra of a) $[M\text{-}5OTf]^{5+}$ and b) $[M\text{-}6OTf]^{6+}$ for assembly **6.**

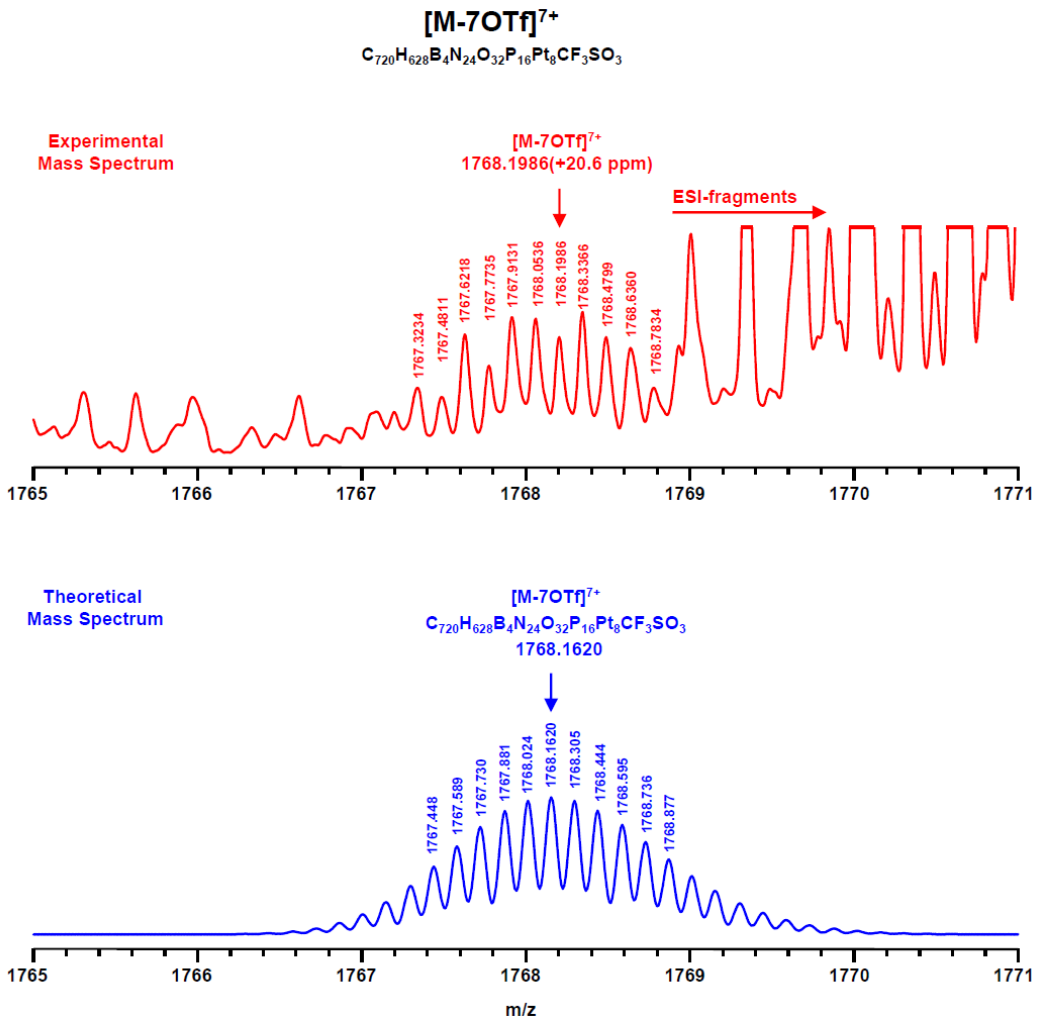


Figure S7. Experimental (red) and theoretical (blue) ESI mass spectra of $[M\text{-}7OTf]^{7+}$ for assembly **4.**

^{1}H DOSY - SPECTRA

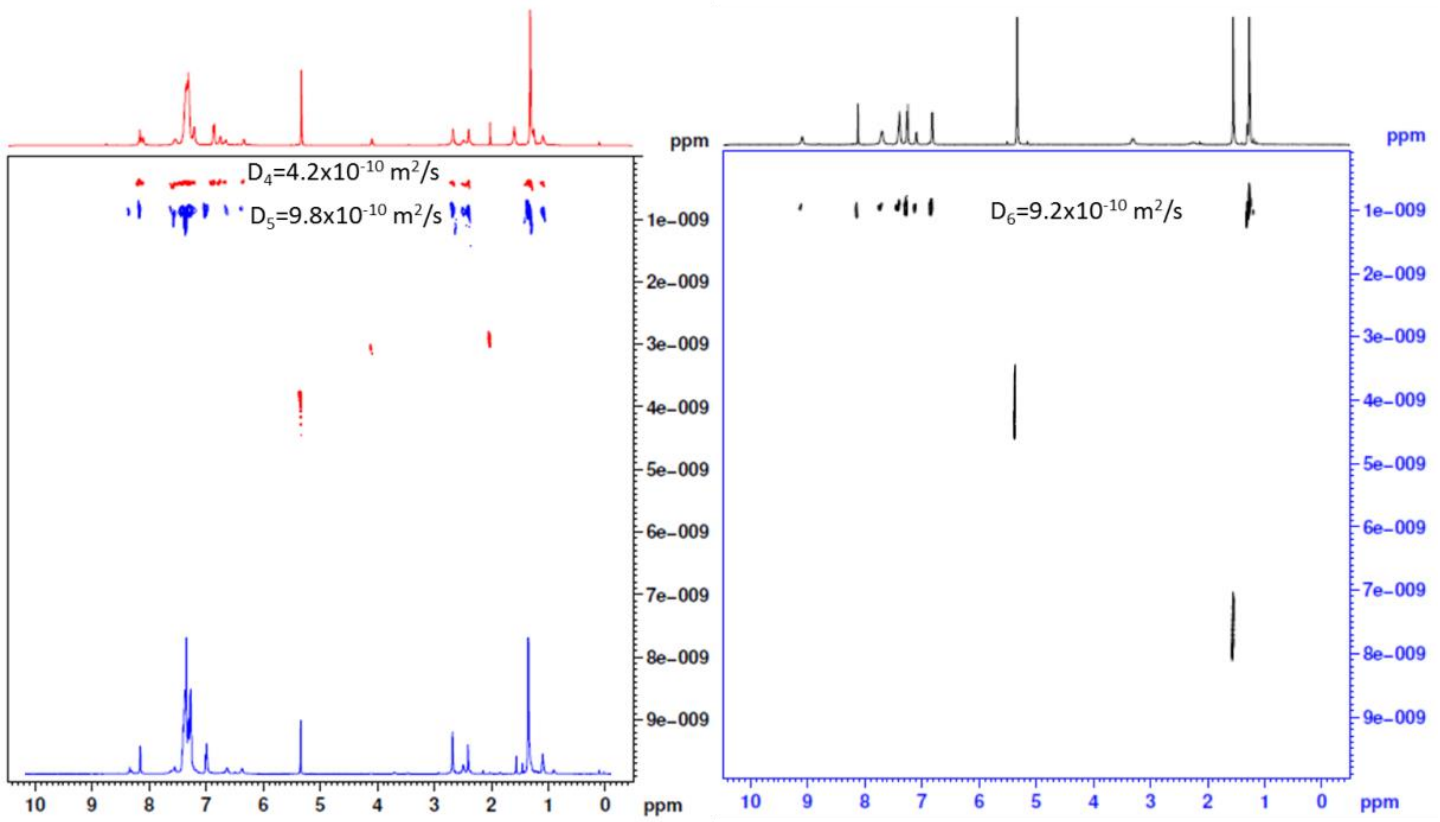


Figure S8. ^{1}H DOSY spectrum of assemblies **4** (red), **5** (blue) and reference compound **6** (black) (500 MHz, CD_2Cl_2, 298 K). The spectra acquisition setup was optimized for the diffusion coefficients of assemblies.

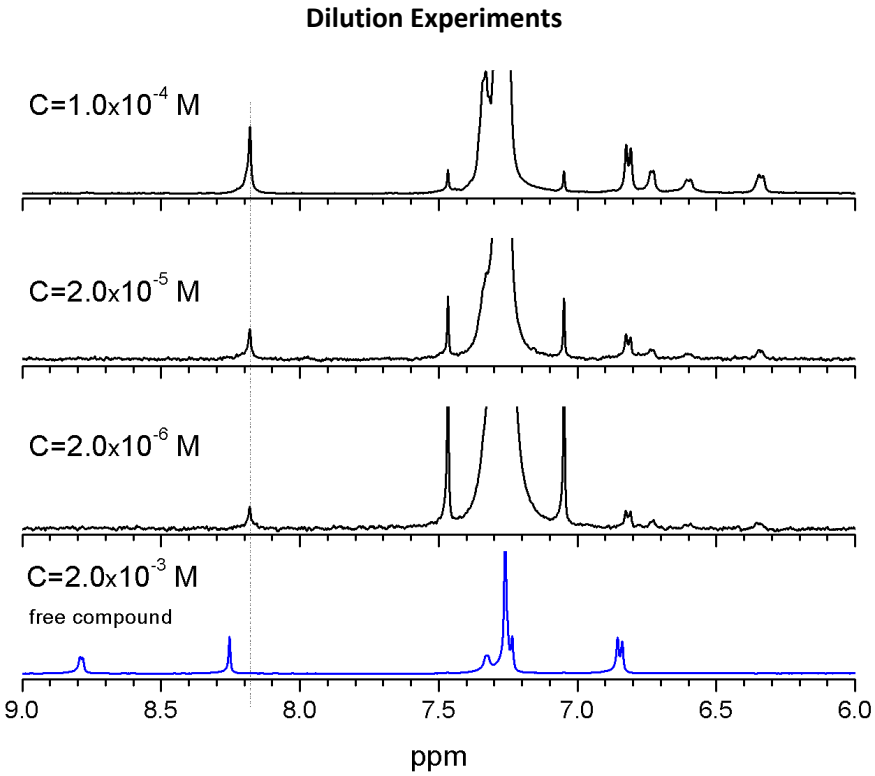


Figure S9. ^{1}H NMR spectra of assembly **4** (black) and free compound **2** (blue) as a function of concentration (500 MHz, $CDCl_3$, 298 K)

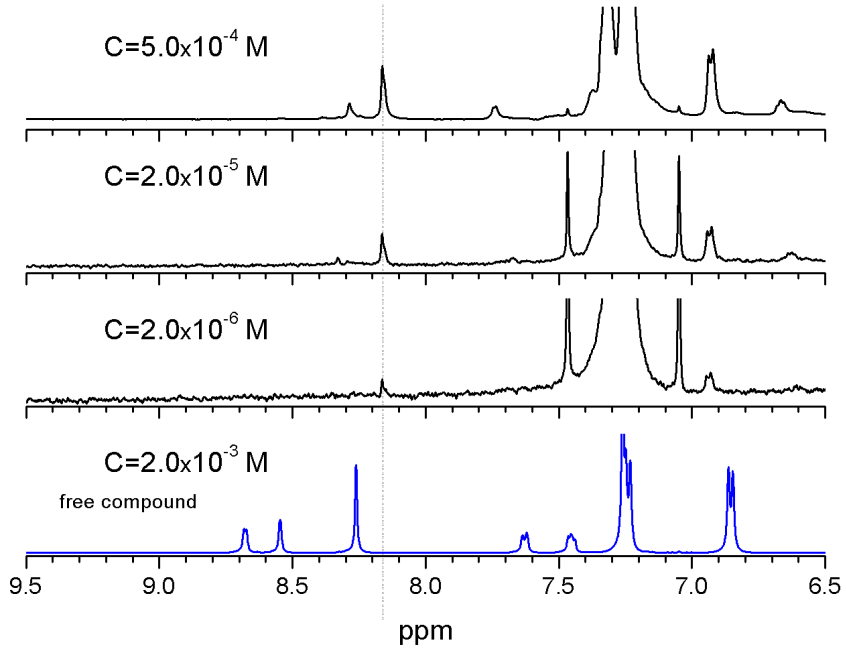


Figure S10. ^{1}H NMR spectra of assembly **5** (black) and free compound **3** (blue) as a function of concentration (500 MHz, $CDCl_3$, 298 K).

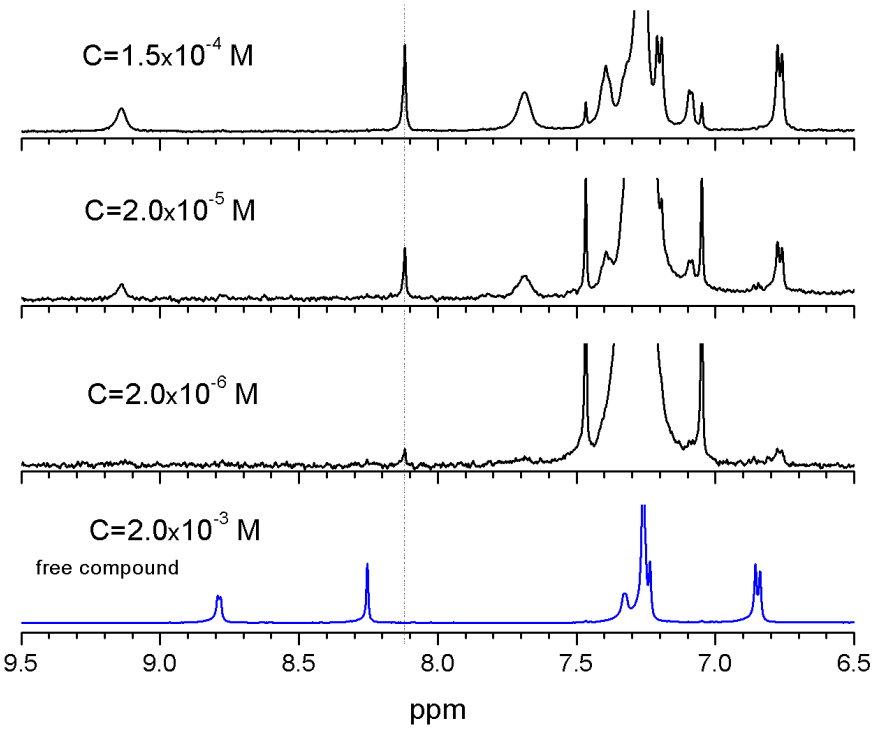


Figure S11. ^{1}H NMR spectra of assembly **6** (black) and free compound **2** (blue) as a function of concentration (500 MHz, $CDCl_3$, 298 K).

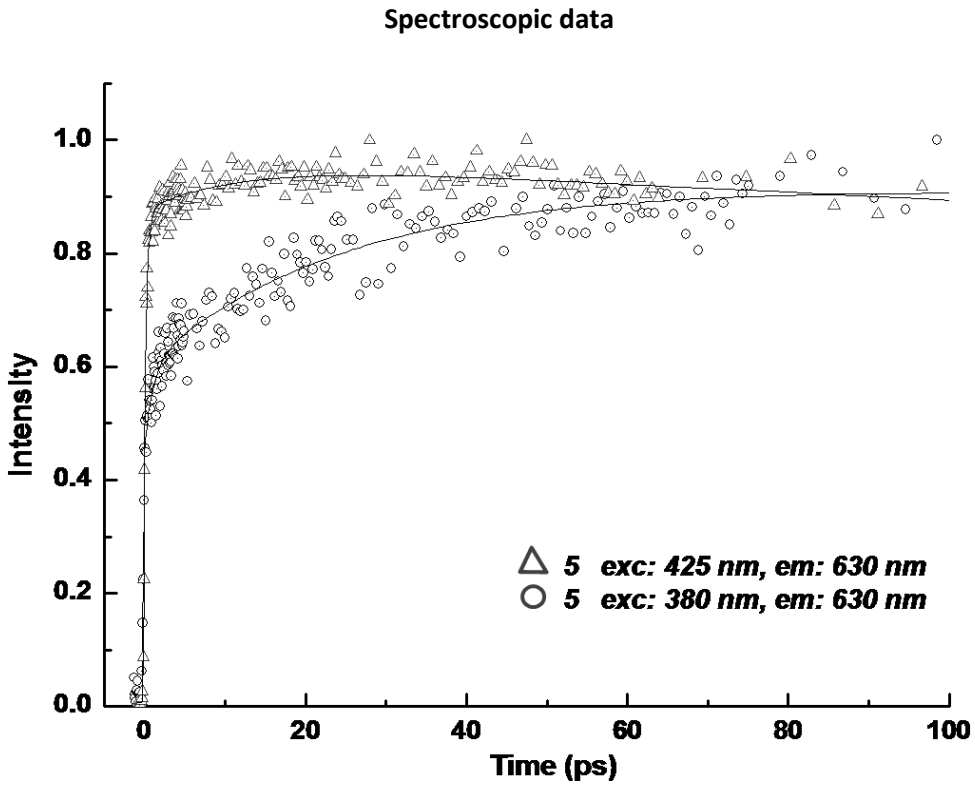


Figure S12. Normalized Fluorescence intensity decays of **3** at 630 nm after excitation at 380 (○) and 425 (Δ) nm in **5**

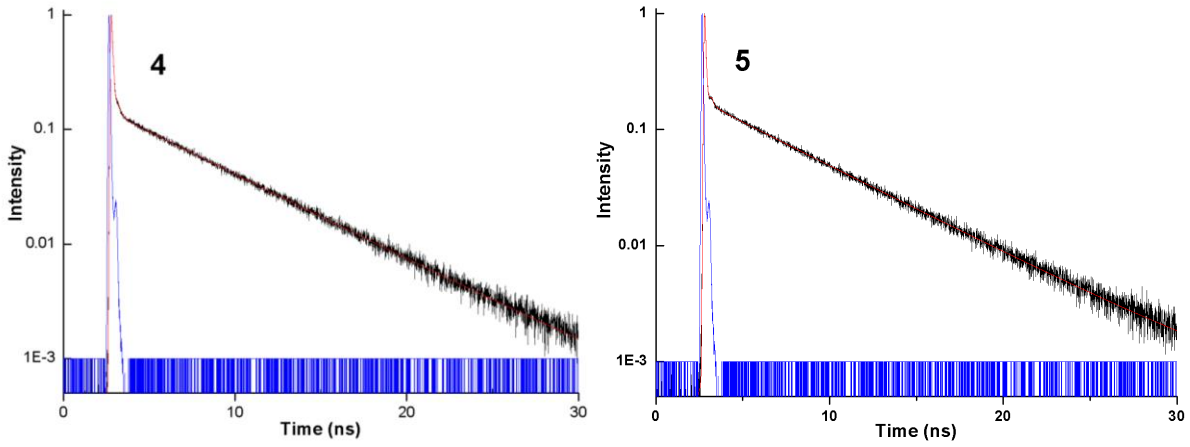


Figure S13. Fluorescence decays of **4** (left) and **5** (right) monitored at 530 nm: Fits are shown with red solid lines; excitation at 470 nm.

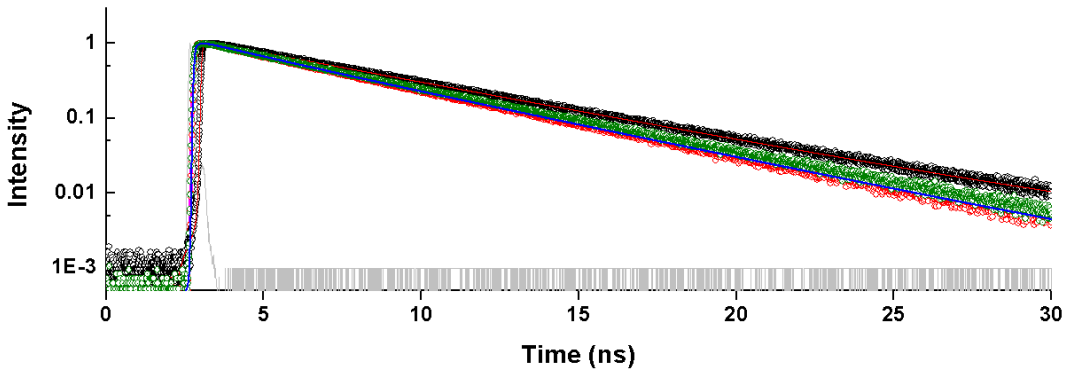


Figure S14. Fluorescence decays of **4** (green), **5** (red) and **6** (black) monitored at 530 nm: Fits are shown with magenta, blue and red solid lines ; excitation at 470 nm.

(1) Baggerman, J.; Jagesar, D. C. ; Vallée, R. A. L.; Hofkens, J.; De Schryver, F. C.; Schelhase, F.; Vögtle, F.; Brouwer, A. M. *Chem. Eur. J.* **2007**, 13, 1291-1299.

(2) Würthner, F.; Thalacker, C.; Sautter, A. *Adv. Mater*. **1999**, 11, 754-758.

(3) Würthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem. Eur. J.* **2001**, 7, 2245-2253.