Supplementary Information

Tunable triphenylamine-based fluorophores for fluorescence quenching detection and identification of nitro-based explosives

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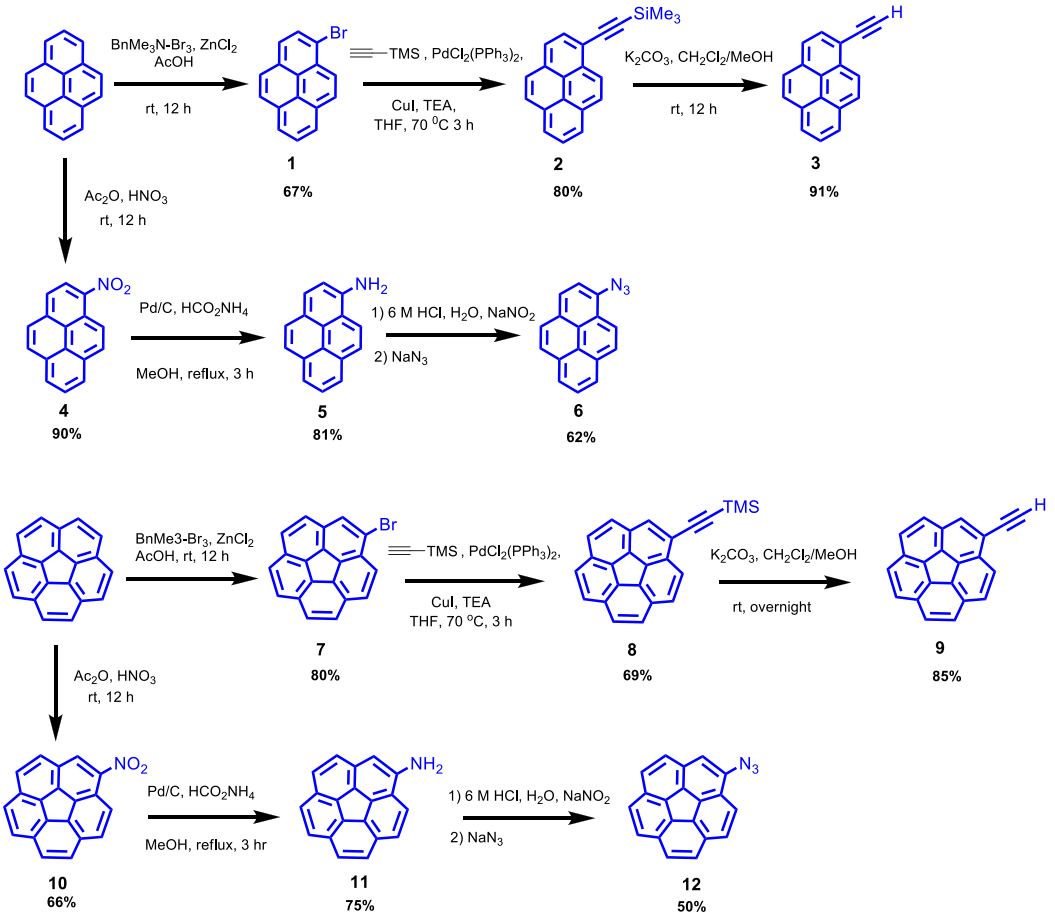
Contents

1. General Information

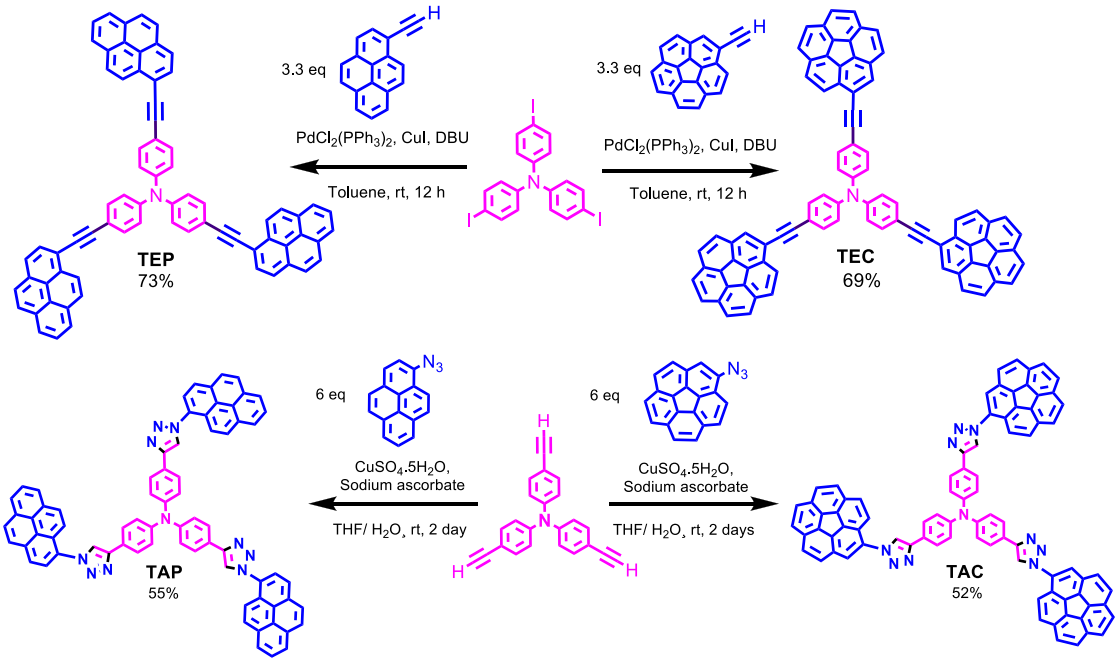
All reagents were purchased from Sigma-Aldrich, Fluka and Acros. Spectroscopic and analytical grade solvent such as chloroform and methylene chloride were used without further purification. Analytical thin layer chromatography was performed on glass-blacked silica gel plates with F254 indicator. Compounds were visualized under UV. Flash chromatography was performed on 70-230 mesh silica gels with commercial grade solvents that were distilled prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 and 500 MHz NMR spectrometers using $CDCl_3$ as solvent unless otherwise noted. All chemical shifts were reported in parts per million (ppm), ^{1}H NMR chemical shifts were referenced to $CDCl_3$ (7.26 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.00 ppm). Multiplicities are reported as s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), etc. UV/vis spectra were measured with dilute aqueous solution in a 10 mm thick quartz using Varian Cary 100 Bio UV-Visible spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS45 spectrofluorometer. Confocal fluorescent images measured Nikon eclipse Ti. The excitation wavelength was maximum wavelength of all fluorophores and the emission was recorded from 390 to 600 nm. Solutions of all fluorophores were prepared in $CHCl_3$. Concentrations of all fluorophores were adjusted to 50 μM and used as stock solutions. All analyst stock solutions were 10 mM and were diluted with $CHCl_3$ until the absorbance at 280 nm (A_{280}) being 0.5. The analyst/fluorophore mixtures were prepared by mixing and $CHCl_3$ dilution to afford the final concentration of fluorophores equal to 0.1 μM and the analyst concentration with $A_{280} = 0.2$.

2. Synthesis scheme of triphenylamine-based fluorophores.



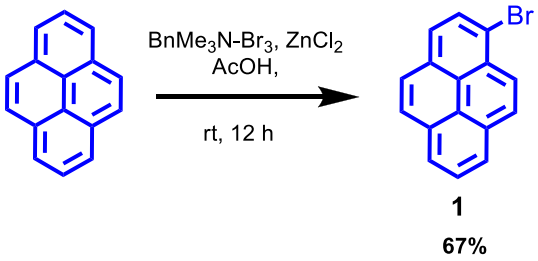
Scheme S1. Synthesis of peripheral groups.



Scheme S2. Synthesis of TEP, TAP, TEC, and TAC.

3. Synthesis procedures and spectroscopic data.

3.1. Synthesis of 1-Bromopyrene (1).

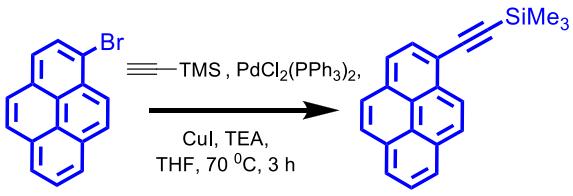


1

67%

To a solution of pyrene (100.2 mg, 0.49 mmol) in glacial acetic acid (15 mL) was added $BTMABr_3$ (198.5 mg, 0.49 mmol), $ZnCl_2$ (72.3 mg, 0.54 mmol). The mixture was stirred for 12 h at room temperature until the initial orange color faded. To the mixture was added water (20 mL) and 5% aq. solution of $NaHSO_3$ (10 mL). The mixture was extracted with hexane (20×4 mL), H_2O, brine, dried $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using pure hexane to give the pure product **1** (92.1 mg; 67%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01-8.24 (m, 8H), 8.58 (d, *J= 12 Hz*, 1H). [9(b)]

3.2. Synthesis of 1-ethynylpyreneTMS (2).

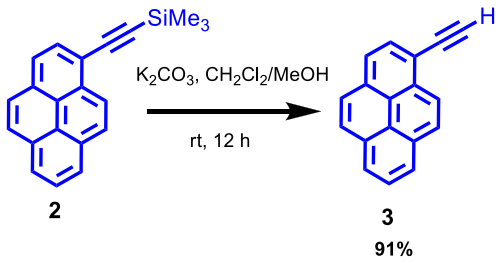


1 **2**

80 %

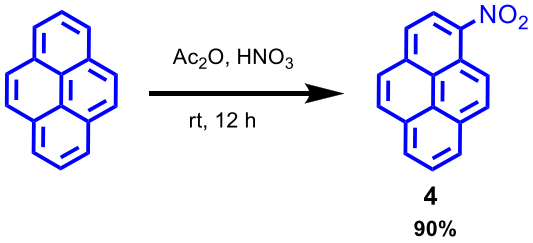
To a mixture of **1** (198.6 mg, 0.71 mmol), $PdCl_2(PPh_3)_2$ (18.9 mg, 0.03 mmol), CuI (5.2 mg, 0.02 mmol), trimethylsilylacetylene (153.0 mg, 1.5 mmol, 0.22 mL) in THF(10 mL) and triethylamine (5 mL) was stirred at 70 °C for 3 h under N_2 atmosphere. The crude mixture was washed with 10% HCl (3×10 mL), and extracted with EtOAc (25 mL), H_2O, brine, dried anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using pure hexane to give the pure product **2** (171.0 mg; 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.43 (s, 9H), 7.99-8.24 (m, 8H), 8.58 (d, *J= 9.0 Hz*, 1H). [9(b)]

3.3. Synthesis of 1-ethynylpyrene (3).



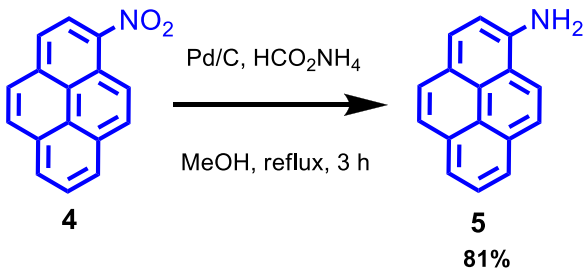
To a mixture of **2** (589.6 mg, 0.2 mmol) and K_2CO_3 (42.5 mg, 0.04 mmol) in CH_2Cl_2 (15 mL) and methanol (15 mL) was stirred at room temperature for 12 h. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL), H_2O, dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The residue was eluted through a silica gel column by pure hexane to give the pure product **3** (407.2 mg; 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.63 (s, 1H), 8.02-8.25 (m, 8H), 8.60 (d, *J= 9.0 Hz*, 1H). [9(b)]

3.4. Synthesis of 1-Nitropyrene (4).



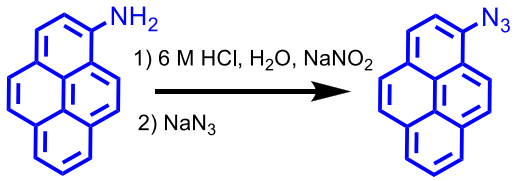
To a mixture of pyrene (5,389.8 mg, 26.7 mmol) in Ac_2O (15 mL, 0.2 mol) was added 65% HNO_3 (1.8 mL, 24.0 mmol). The mixture was stirred at room temperature for 12 h and a thick yellow precipitate formed. The mixture were filtered off and then the crude product obtained on evaporation of the solvent was purified on a silica gel column using gradient solvents from pure hexane to hexane: CH_2Cl_2 (3:1) to give the pure product **4** (5,9320 mg; 90%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99-8.27 (m, 7H), 8.59 (d, *J= 8.0 Hz*, 1H), 8.79 (d, *J= 8.0 Hz*, 1H). [12]

3.5. Synthesis of 1-Aminopyrene (5).



A solution of **4** (86.5 mg, 0.35 mmol) and HCO_2NH_4 (440.9 mg, 7.2 mmol), and Pd/C (60.4 mg, 0.06 mmol) in 50 mL of absolute MeOH was heated at reflux for 3 h in N_2. The mixture was worked up by H_2O and extracted with CH_2Cl_2 (30×2 mL), H_2O, brine, anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using gradient solvents from pure hexane to a mixture of hexane: CH_2Cl_2 (1:1) to give the pure product **5** (61.8 mg; 81%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.53 (br, 2H), 7.41 (d, *J= 8.2 Hz*, 1H), 7.84 (d, *J= 8.9 Hz*, 1H), 7.93-8.09 (m, 7 *Hz*).[12]

3.6. Synthesis of 1-Azopyrene (6).

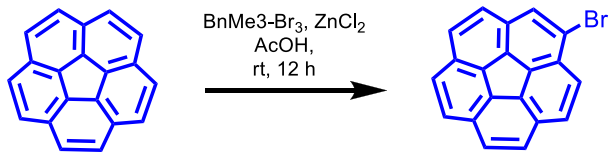


5 **6**

62%

The mixture of **5** (451.4 mg, 2.10 mmol) in 6 M HCl 10 mL was heated to 70 °C for 20 min and stirred until having colorless precipitates, and then cooled to 0-5 °C in an ice bath. To this stirred suspension in water 5 mL of $NaNO_2$ (180.9 mg, 2.60 mmol) in water 5 mL, the mixture was allowed to stir for 30 min after completion of the addition. This diazonium solution was then slowly added to a solution of NaN_3 (171.2 mg, 2.70 mmol) in H_2O 10 mL. A total of 2 h after completion of the addition, the dark brown mixture was extracted with ether (3×20 mL), H_2O, brine, dried $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using pure hexane to give the pure product **6** (316.4 mg; 62%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J= 12 Hz*, 1H), 7.99-8.03 (m, 3H), 8.08 (d, *J= 12 Hz*, 1H), 8.16-8.18 (m, 3H)), 8.29 (d, *J= 8 Hz*, 1H). [12]

3.7 Synthesis of 1-Bromocorannulene (7).



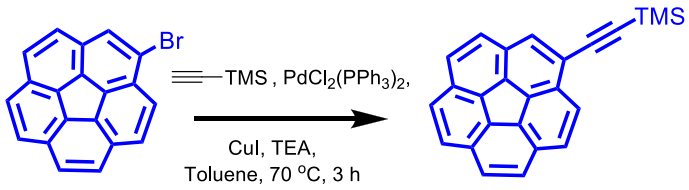
7

80%

To a solution of corannulene (49.2 mg, 0.20 mmol) in glacial acetic acid (15 mL) was added $BTMABr_3$ (77.8 mg, 0.20 mmol), $ZnCl_2$ (32.6 mg, 0.23 mmol). The mixture was

stirred for 12 h at room temperature until the initial orange color faded. To the mixture was added water (20 mL) and 5 % aq solution of $Na_2S_2O_3$ (10 mL). The mixture was extracted with hexane (20×4 mL), H_2O, brine, dried $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using pure hexane to give the pure product **7** (52.9 mg; 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, *J= 8.0 Hz*, 1H), 7.80-7.84 (m, 5H), 7.89 (d, *J= 8.0 Hz*, 1H), 7.95 (d, *J= 8.0 Hz*, 1H), 8.04 (S, 1H).[10]

3.8 Synthesis of ethynylcorannuleneTMS (8).

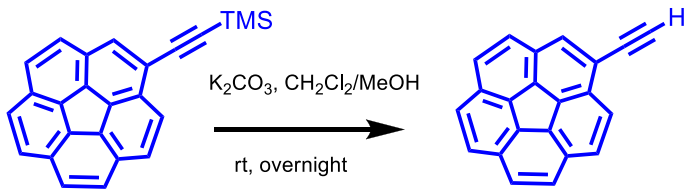


7 **8**

69%

To a mixture of **7** (198.2 mg, 0.60 mmol), $PdCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol), CuI (5.1 mg, 0.02 mmol), trimethylsilyl acetylene (153 mg, 1.50 mmol, 0.22 mL) in THF (10 mL) and triethylamine (5 mL) was stirred at 70 °C for 3 h. The crude mixture was washed with 10% HCl (3×10 mL), and extracted with EtOAc (25 mL), H_2O, brine, dried anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using pure hexane to give the pure product **8** (139.1 mg; 69%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.35 (s, 9H), 7.77-7.87 (m, 6H), 8.01 (s, 1H), 8.03 (d, *J= 12 Hz*, 1H).[10]

3.9 Synthesis of 1-ethynylcorannulene (9).



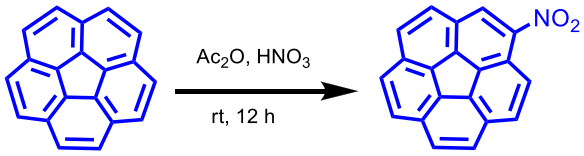
8 **9**

85%

To a mixture of **5** (50.8 mg, 0.15 mmol) and K_2CO_3 (4.7 mg, 0.03 mmol) in CH_2Cl_2 (15 mL) and methanol (15 mL) was stirred at room temperature for overnight. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL), H_2O, dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The residue was eluted through a silica gel column by pure hexane to give the pure product **6** (34.2 mg; 85%) as a

white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.43 (s, 1H), 7.77 (d, *J= 12.0 Hz*, 1H), 7.81-7.83 (m, 5H), 7.88 (d, *J= 8.0 Hz*, 1H), 8.05-8.07 (m, 2H). [10]

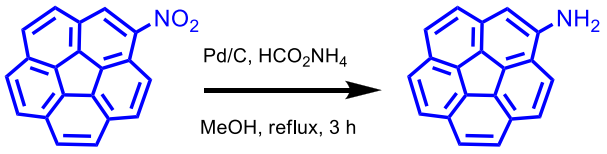
3.10 Synthesis of 1-Nitrocorannulene (10).



10
66%

To a mixture of corannulene (1.0982 g, 4.40 mmol) in Ac_2O (5.0 mL, 0.08 mol) was added 65% HNO_3 (0.3 mL, 4.4 mmol). The mixture was stirred at room temperature for 12 h and a thick yellow precipitate formed. The mixture were filtered off and then the crude product obtained on evaporation of the solvent was purified on a silica gel column using gradient solvents from pure hexane to hexane:CH_2Cl_2 (3:1) to give the pure product **10** (0.8551 g; 66%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81-7.90 (m, 6H), 7.97 (d, *J= 8.0 Hz*, 1H), 8.53 (d, *J= 8.0 Hz*, 1H), 8.95 (s, 1H).[13]

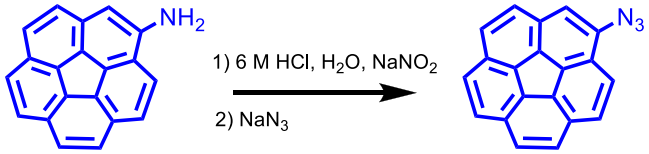
3.11 Synthesis of 1-Aminocorannulene (11).



10 **11**
75%

A solution of **10** (202.5 mg, 0.68 mmol), HCO_2NH_4 (880.0 mg, 14.00 mmol), and Pd/C (122.0 mg, 0.12 mmol) in 50 mL of absolute MeOH was heated at reflux for 3 h in N_2. The mixture was worked up by H_2O and extracted with CH_2Cl_2 (30×2 mL), H_2O, brine, dried anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using gradient solvents from pure hexane to a mixture of hexane:CH_2Cl_2 (1:2) to give the pure product **11** (139.3 mg; 75%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.49 (br, 2H), 6.83 (s, 1H), 7.59 (d, *J= 8.0 Hz*, 1H), 7.70-7.83 (m, 7 Hz).[13]

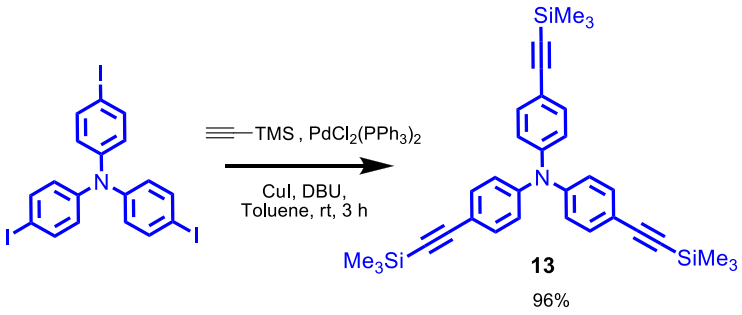
3.12 Synthesis of 1-Azocorannulene (12).



11 **12**
50%

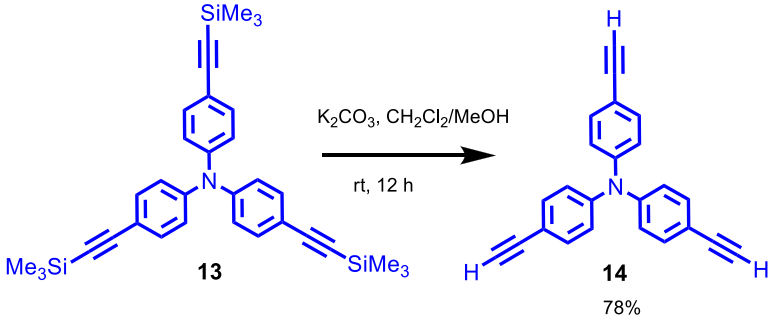
The mixture of **11** (101.2 mg, 0.38 mmol) in 6 M HCl 10 mL was heated to 70 °C for 20 min and stirred until having colorless precipitates, and then cooled to 0-5 °C in an ice bath. Next added $NaNO_2$ (3.058 g, 43.00 mmol), the mixture was allowed to stir for 30 min after completion of the addition. This diazonium solution was then slowly added to NaN_3 (1.1043 g, 15.00 mmol). A total of 2 h after completion of the addition, the dark brown mixture was extracted with ether (3×20 mL), H_2O, brine, dried $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using pure hexane to give the pure product **12** (56.0 mg; 50%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45 (s, 1H), 7.74 (d, *J= 8.0 Hz*, 1H), 7.79-7.85 (m, 6H), 7.92 (d, *J= 8.0 Hz*, 1H).[13]

3.13. Synthesis of triphenylamineTMS (13).



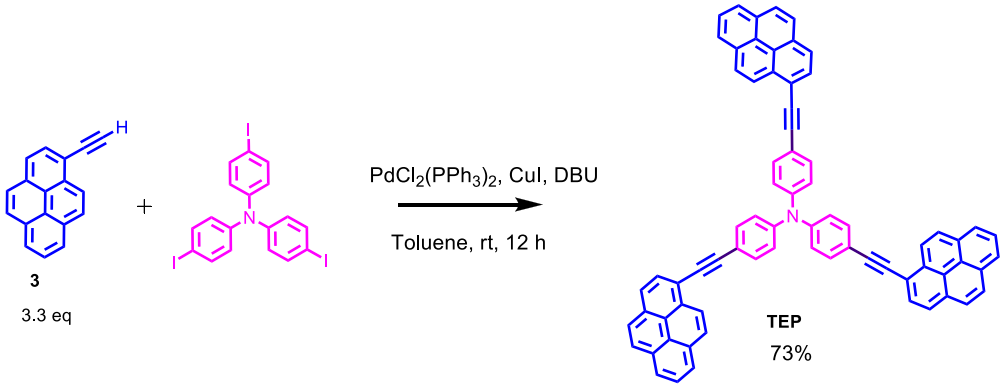
To a mixture of Triiodotriphylamine (2.1094 g, 3.40 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.08 mmol), CuI (15.0 mg, 0.08 mmol), trimethylsilyl acetylene (1.04 g, 10.50 mmol, 1.5 mL) in toluene (40 mL) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (5 mL) was stirred at room temperature for 3 h. The crude mixture was washed with 10% HCl (3×10 mL), and extracted with EtOAc (25 mL), H_2O, brine, dried anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was eluted through a silica gel column using gradient solvents from pure hexane to a mixture of hexane:CH_2Cl_2 (4:1) to give the pure product **13** (1.7362 g; 96%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.24 (s, 27H), 6.96 (d, *J= 8.8 Hz*, 6H) 7.34 (d, *J= 8.8 Hz*, 6H).[11]

3.14. Synthesis of 14.



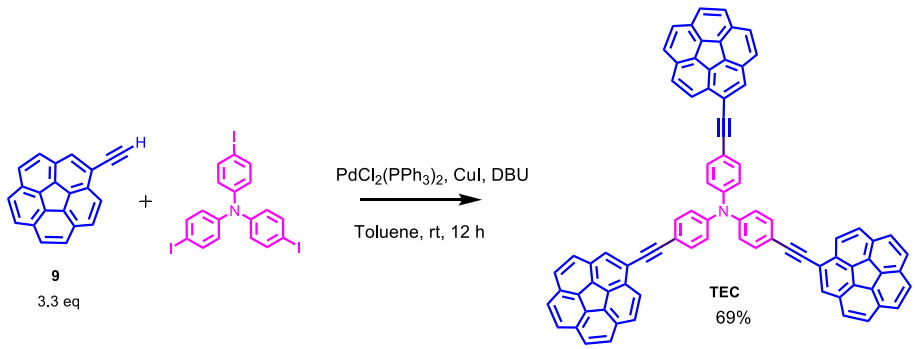
To a mixture of **13** (1.5955 g, 3.0 mmol) and K_2CO_3 (171.2 mg, 1.5 mmol) in CH_2Cl_2 (20 mL) and methanol (20 mL) was stirred at room temperature for 12 h. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×40 mL), H_2O, dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The residue was eluted through a silica gel column using gradient solvents from pure hexane to a mixture of hexane:CH_2Cl_2 (4:1) to give the pure product **14** (0.7397 g; 78%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.05 (s, 3H), 7.02 (d, *J= 8.8 Hz*, 6H), 7.38 (d, *J= 8.8 Hz*, 6H).[11]

3.15. Synthesis of triphenylamine triethynylene pyrene (TEP).



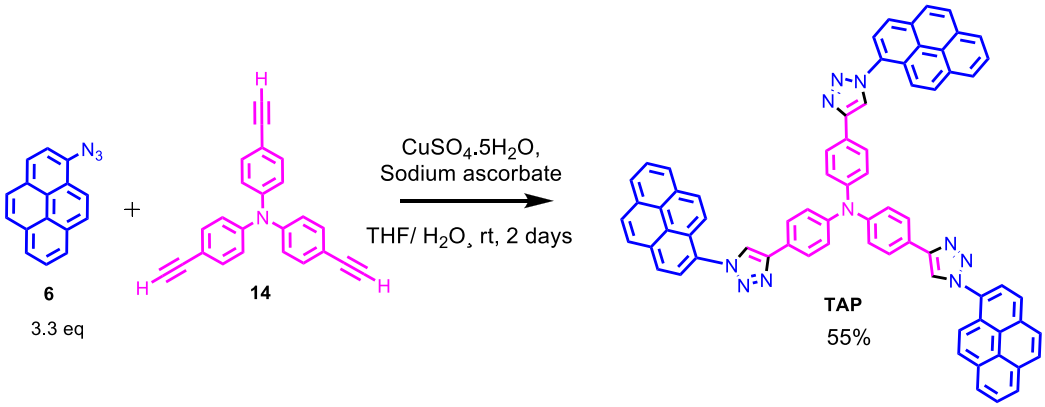
To a mixture of Triiodotriphylamine (82.7 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (20.4 mg, 0.03 mmol), CuI (5.1 mg, 0.02 mmol), **3** (117.4 mg, 0.51 mmol) in toluene (20 mL) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.5 mL) was stirred at room temperature for 12 h. After removing the solvent under vacuum, the residue was eluted through a silica gel column using gradient solvents from pure hexane, a mixture of hexane:CH_2Cl_2 (3:1), pure CH_2Cl_2, and CH_2Cl_2:THF (10:1) to give the pure product **TEP** (89.0 mg; 73%) as a yellow solid: mp; 233-234^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27 (d, *J= 8.0 Hz*, 6H), 7.70 (d, *J= 8.0 Hz*, 6H), 8.03-8.26 (m, 24H), 8.70 (d, *J= 8.0 Hz*, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 88.7, 95.1, 118.0, 118.4, 124.3, 124.4, 124.6, 125.6(2), 126.3, 127.3, 128.1, 128.3, 129.6, 131.1, 131.2, 131.3, 131.9, 133.0, 146.9. MALDI-TOF m/z Calcd for $C_{72}H_{39}N$ $[M]^+$: 917.3; Found: 917.2 [M]+: HRMS m/z Calcd for $C_{72}H_{40}N$ $[M+H]^+$: 918.3155 Found: 918.3143 $[M+H]^+$.

3.16. Synthesis of triphenylamine triethynylene corannulene (TEC).



To a mixture of Triiodotriphylamine (47.2 mg, 0.08 mmol), $PdCl_2(PPh_3)_2$ (10.0 mg, 0.01 mmol), CuI (2.0 mg, 0.01 mmol), **9** (72.5 mg, 0.30 mmol) in toluene (30 mL) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.5 mL) was stirred at room temperature for 12 h. After removing the solvent under vacuum, the residue was eluted through a silica gel column using gradient solvents from pure hexane, a mixture of hexane:CH_2Cl_2 (3:1), pure CH_2Cl_2, and CH_2Cl_2:THF (10:1) to give the pure product **TEC** (55.8 mg; 69%) as a yellow solid: mp; 214-215°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27 (d, *J= 8.0 Hz*, 6H), 7.70 (d, *J= 8.0 Hz*, 6H), 8.03-8.26 (m, 24H), 8.70 (d, *J= 8.0 Hz*, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 88.7, 95.1, 118.0, 118.4, 124.3, 124.4, 124.6, 125.6(2), 126.3, 127.3, 128.1, 128.3, 129.6, 131.1, 131.2, 131.3, 131.9, 133.0, 146.9. MALDI-TOF m/z Calcd for $C_{84}H_{39}N$ $[M]^+$: 1061.3; Found: 1061.1 [M]+: HRMS m/z Calcd for $C_{84}H_{40}N$ $[M+H]^+$: 1062.3155 Found: 1062.3148 $[M+H]^+$.

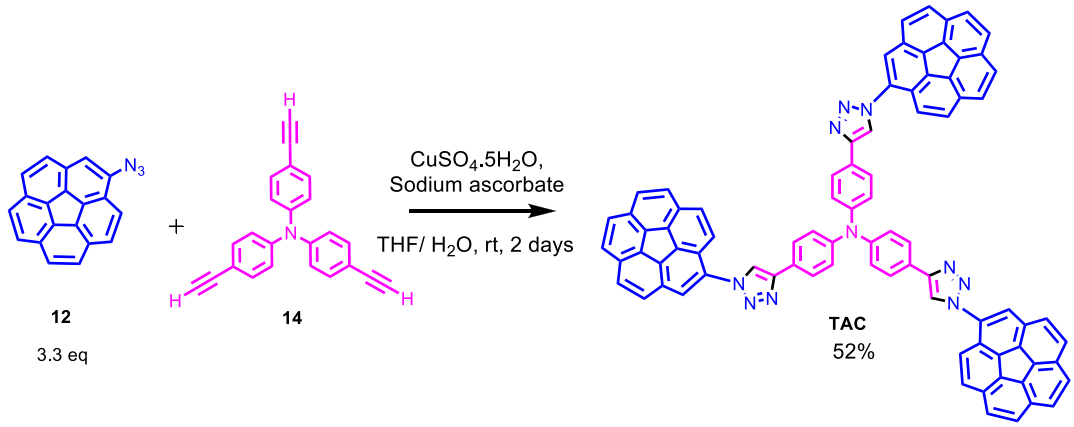
3.17. Synthesis of triphenylamine triazole pyrene (TAP).



To a solution of **14** (7.2 mg , 0.023 mmol) and 1-Azopyrene (47.0 mg, 0.19 mmol) in THF (5 mL), a solution of $CuSO_4 \cdot 5H_2O$ (8.6 mg, 0.034 mmol) in water (2.5 mL) was added. Then, a freshly prepared solution of sodium ascorbate (10.9 mg, 0.14 mmol), in water (2.5 mL) was added dropwise and the reaction mixture was stirred for 2 days at room temperature. After removing the THF under vacuum, dichloromethane (20×2 mL) and an aqueous solution of ammonia (15%) were added (20 mL). The mixture was stirred for 10 min to remove all the Cu(I) derivative, trapped inside the product as $[Cu(NH_3)_6]^+$. The organic phase was washed twice with water (2×100 mL). The solvent was removed under vacuum and the product was purified by column chromatography using gradient solvents from pure hexane, a mixture of hexane:CH_2Cl_2 (1:1), pure CH_2Cl_2, and CH_2Cl_2:THF (10:1) to give the pure product **TAP** (14.3 mg; 55%) as a brown solid: mp; 173-174°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J= 8.0 Hz*, 6H), 7.97-8.01 (m, 9H), 8.10-8.33 (m, 27H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 121.4, 122.6, 123.6, 124.5, 124.9, 125.0, 125.4, 125.5, 126.4, 126.5, 126.7, 127.1, 127.3, 127.4, 129.3, 130.0, 131.0, 131.4, 132.6, 147.7, 147.9. MALDI-TOF m/z Calcd for

$C_{72}H_{42}N_{10}$ $[M]^+$: 1046.4; Found: 1046.1$[M]^+$: HRMS m/z Calcd for $C_{72}H_{43}N_{10}$ $[M+H]^+$: 1047.3667 Found: 1047.3668 $[M+H]^+$.

3.18. Synthesis of triphenylamine triazole corannulene (TAC).



To a solution of **14** (6.0 mg, 0.02 mmol) and **12** (35.6 mg, 0.12 mmol) in THF (5 mL), a solution of $CuSO_4 \cdot 5H_2O$ (9.0 mg, 0.03 mmol) in water (2.5 mL) was added. Then, a freshly prepared solution of sodium ascorbate (12 mg, 0.14 mmol), in water (2.5 mL) was added dropwise and the reaction mixture was stirred for 2 days at room temperature in the dark. After removing the THF under vacuum, dichloromethane (20×2 mL) and an aqueous solution of ammonia (15%) were added (20 mL). The mixture was stirred for 10 min to remove all the Cu(I) derivative, trapped inside the product as $[Cu(NH_3)_6]^+$. The organic phase was washed twice with water (2×100 mL). The solvent was removed under vacuum and the product was purified by column chromatography using gradient solvents from pure hexane, a mixture of hexane:CH_2Cl_2 (1:1), pure CH_2Cl_2, and CH_2Cl_2:THF (10:1) to give the pure product **TAC** (12 mg; 52%) as a brown solid: mp; 175-176°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J= 8.0 Hz*, 6H), 7.87-8.01 (m, 27H), 8.19 (s, 3H), 8.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 110.0, 120.8, 124.6, 124.7, 124.8, 125.5, 127.0, 127.2, 127.4, 127.8, 128.1, 128.2, 128.7, 129.9, 131.2(2), 131.3, 131.4, 135.3, 135.5(2), 136.2, 136.4, 147.5. MALDI-TOF m/z Calcd for $C_{84}H_{42}N_{10}$ $[M]^+$: 1190.4; Found: 1190.2 $[M]^+$: HRMS m/z Calcd for $C_{84}H_{43}N_{10}$ $[M+H]^+$: 1191.3667 Found: 1191.3664 $[M+H]^+$.

4. ^{1}H, ^{13}C- NMR and mass spectrum of synthesized compounds**.**

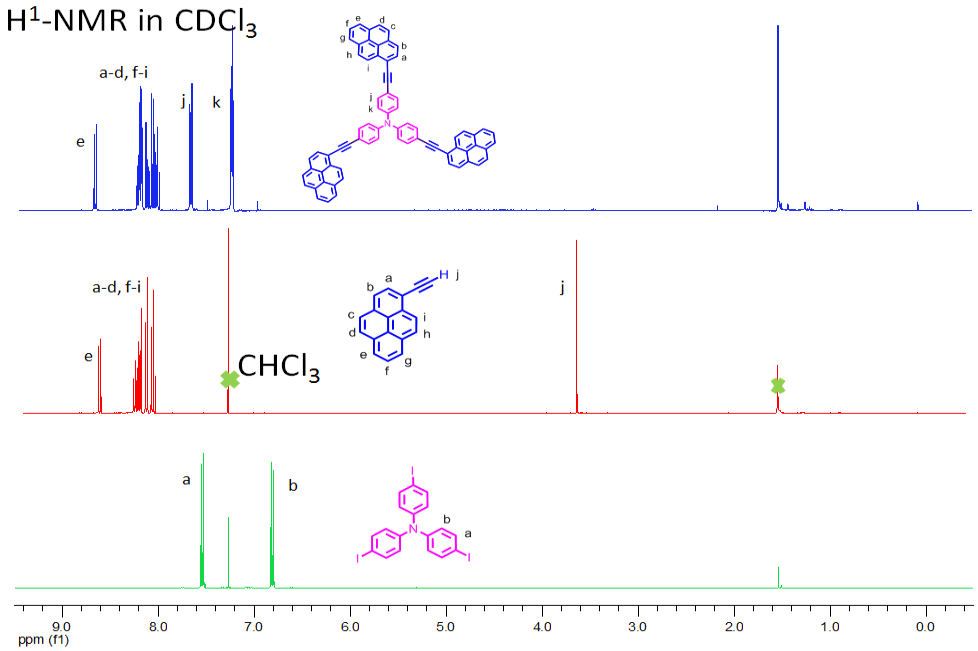


Fig. S4.1 Stacked plot of the ^{1}H-NMR (400 MHz) spectra of **TI_3**, **3**, and **TEP** in $CDCl_3$.

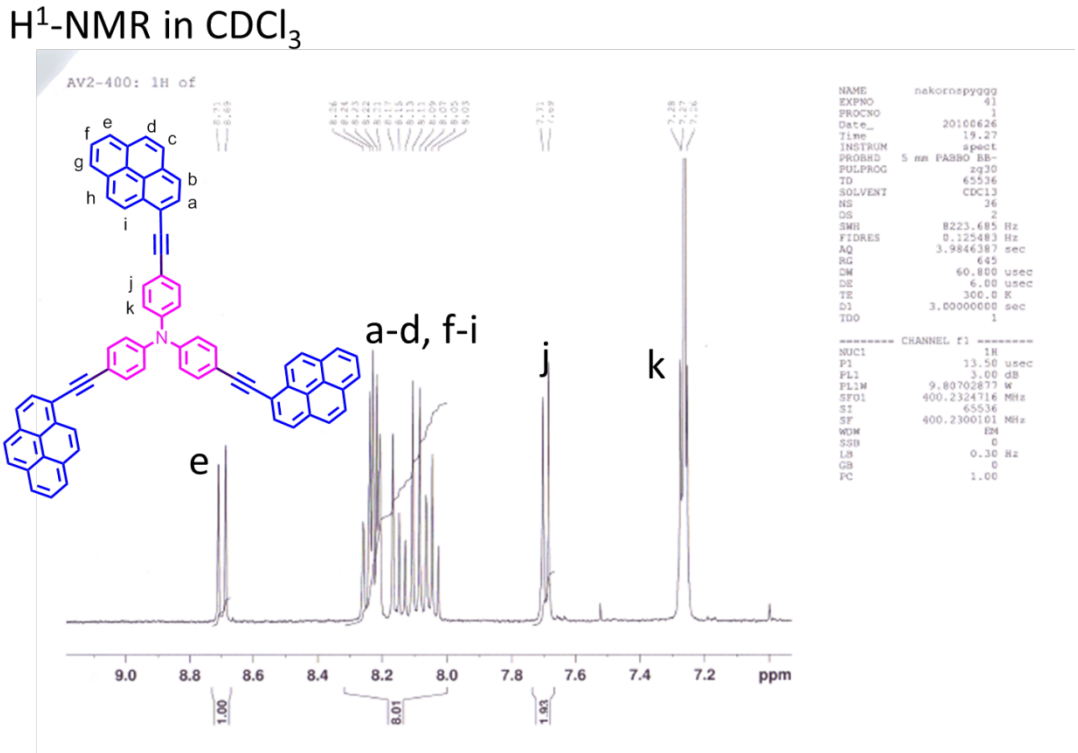


Fig. S4.2 ^{1}H-NMR (400 MHz) spectrum of **TEP**.

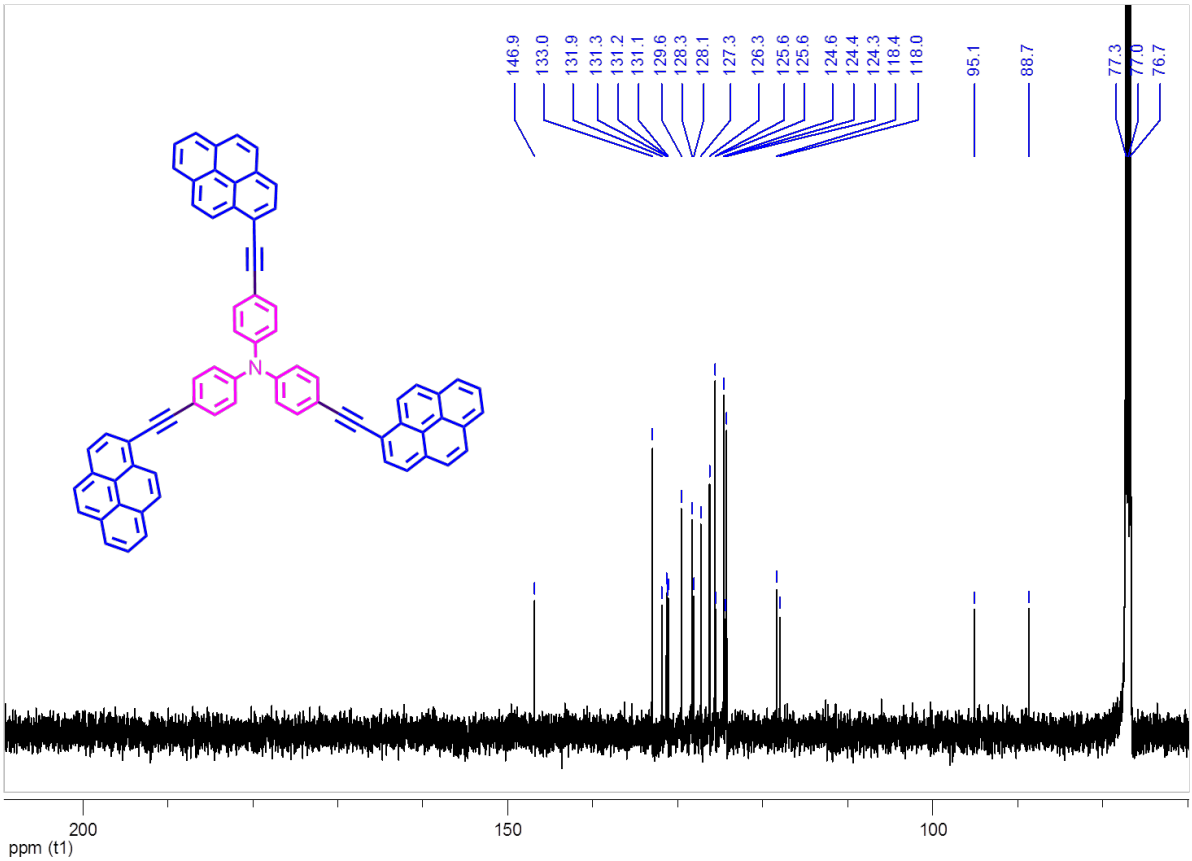


Fig. S4.3 ^{13}C-NMR (100 MHz) spectrum of **TEP**.

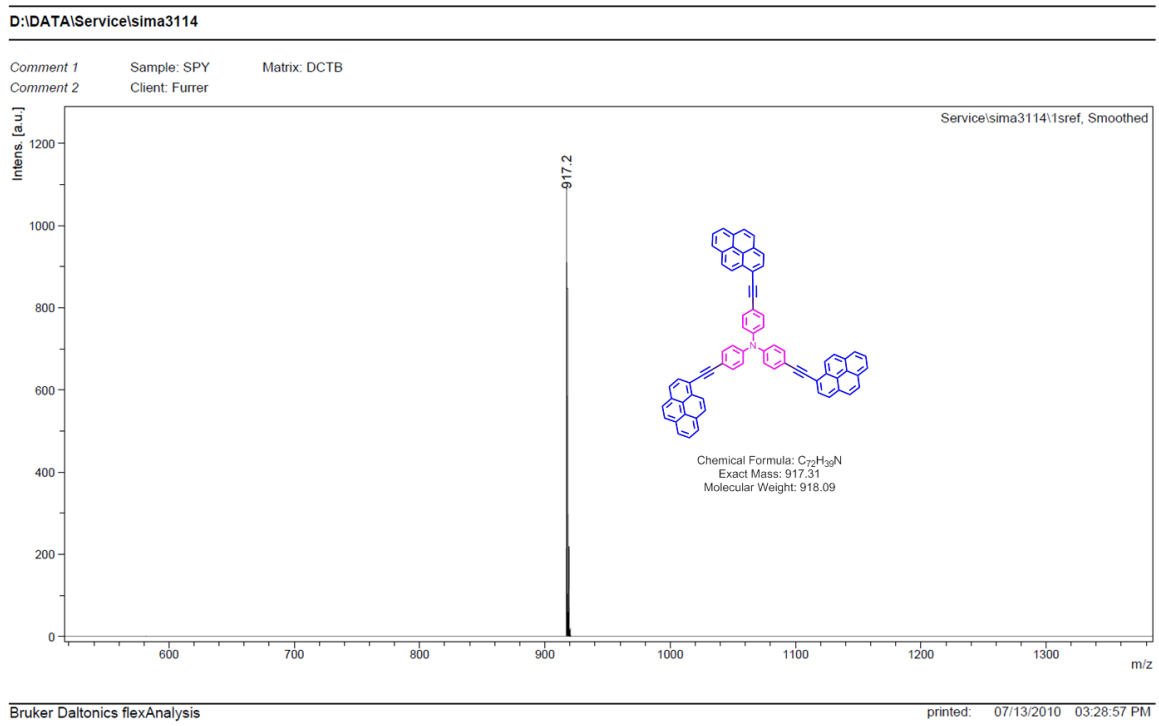


Fig. S4.4 MALDI-TOF-MS spectrum of **TEP**.

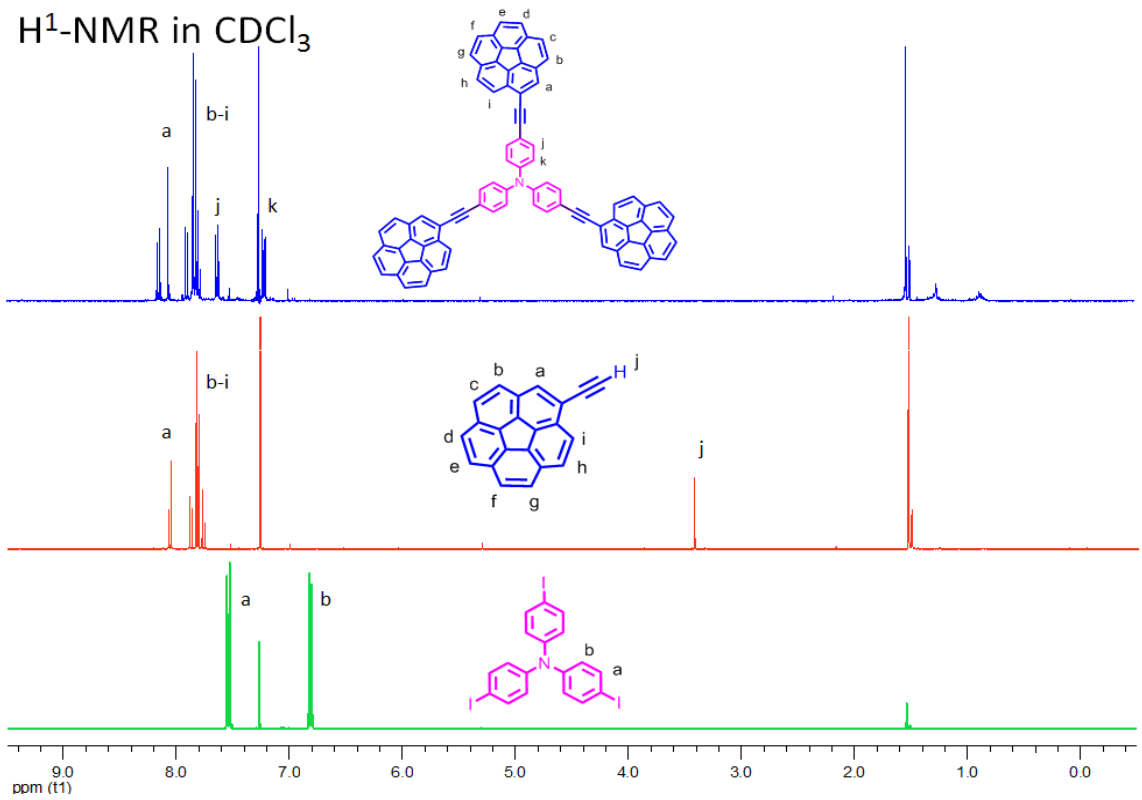


Fig. S4.5 Stacked plot of the ^{1}H-NMR (400 MHz) spectra of **TI_3**, **9**, and **TEC** in $CDCl_3$.

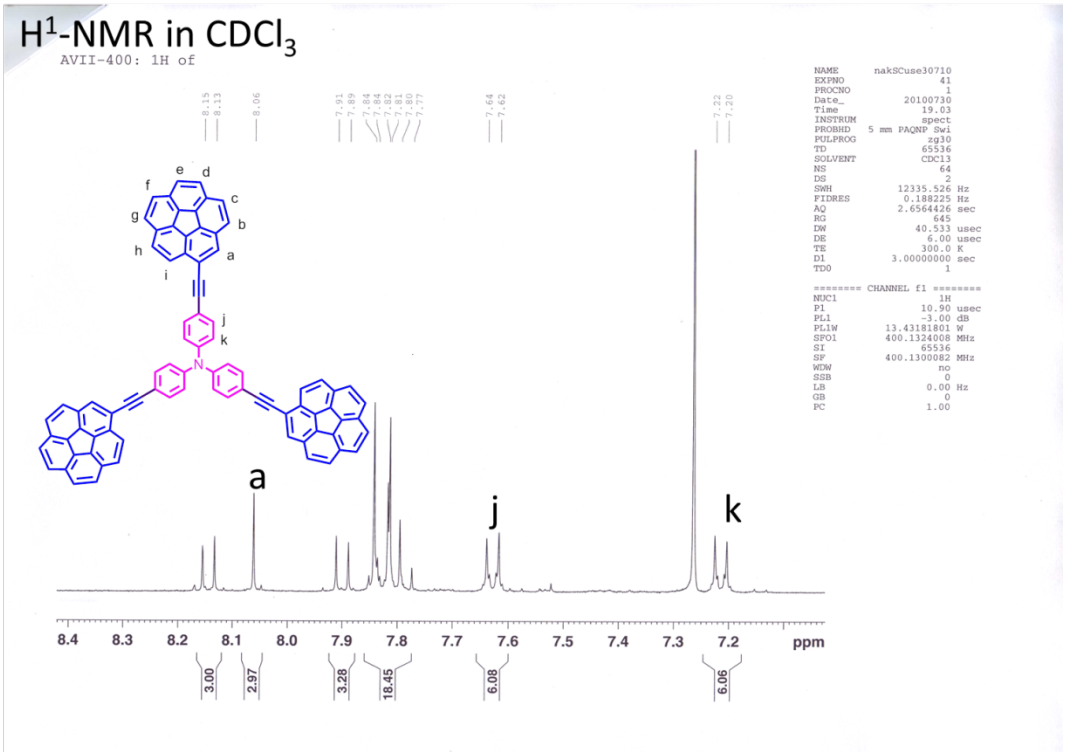


Fig. S4.6 ^{1}H-NMR (400 MHz) spectrum of **TEC**.

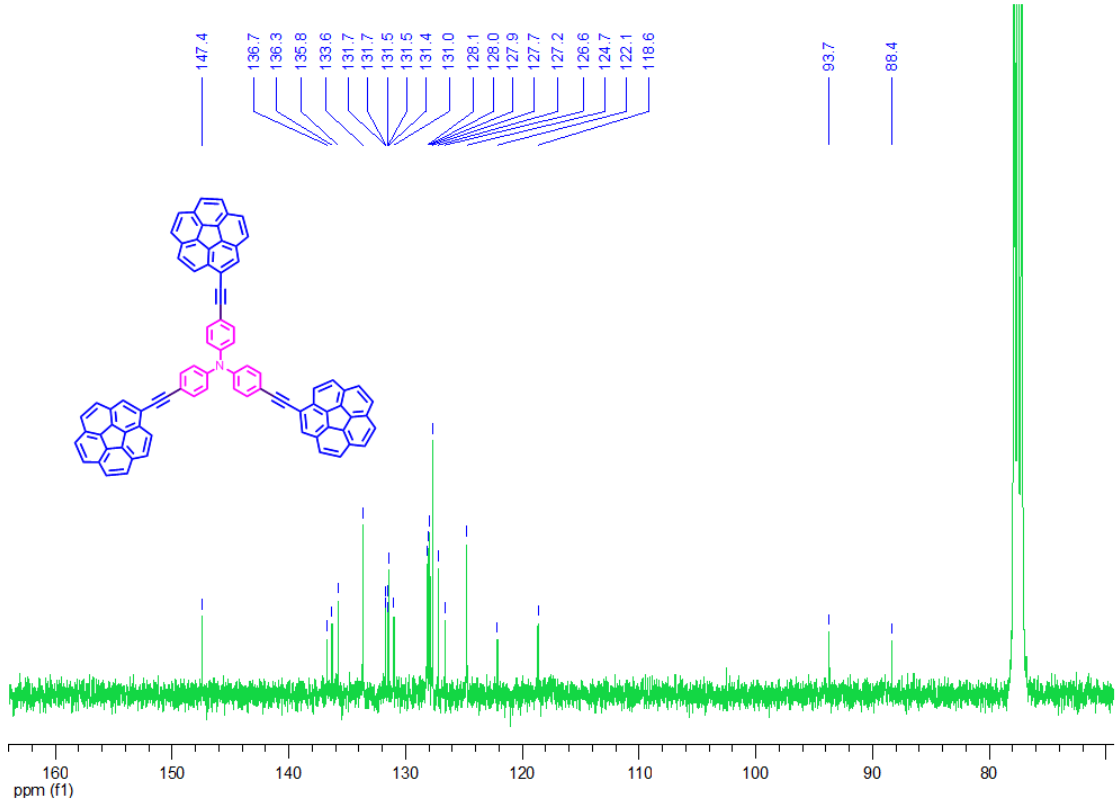


Fig. S4.7 ^{13}C-NMR (100 MHz) spectum of **TEC**.

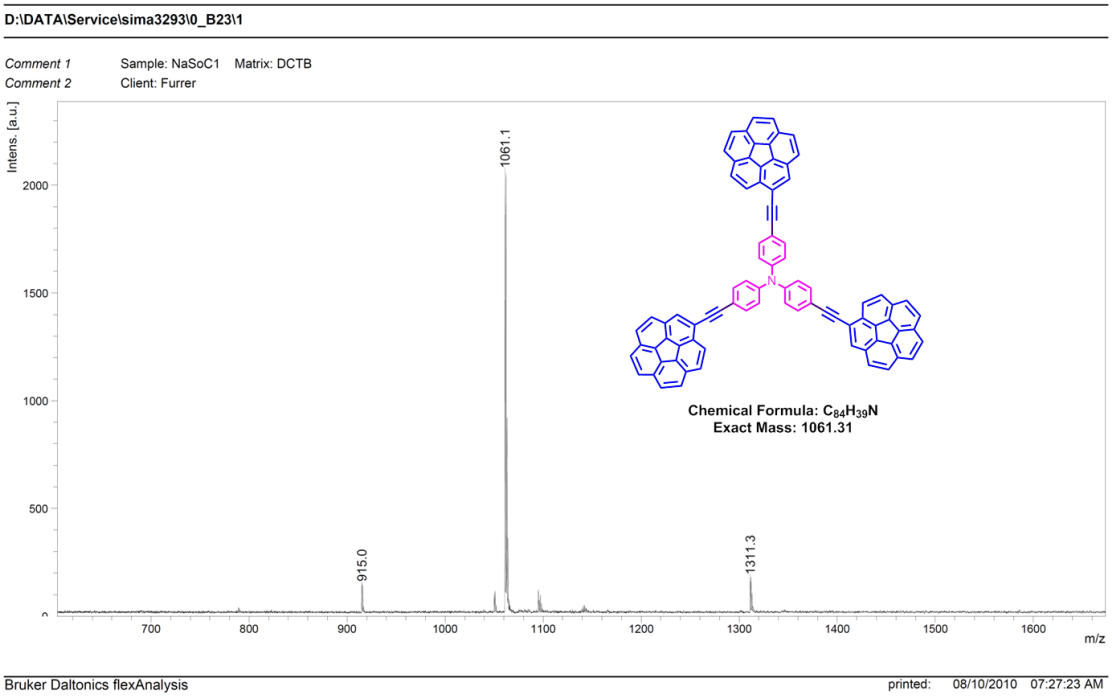


Fig. S4.8 MALDI-TOF-MS spectrum of **TEC**.

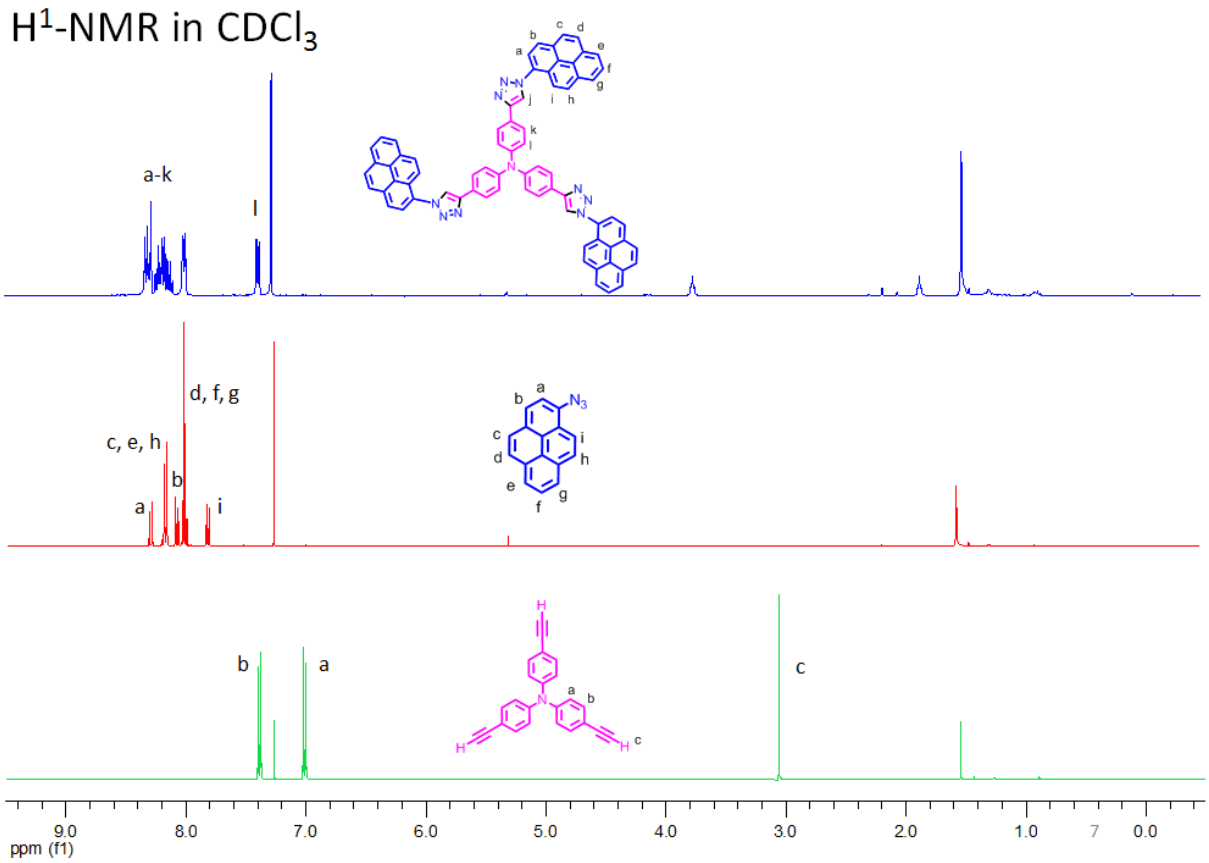


Fig. S4.9 Stacked plot of the ^{1}H-NMR (400 MHz) spectra of **14**, **9**, and **TAP** in $CDCl_3$.

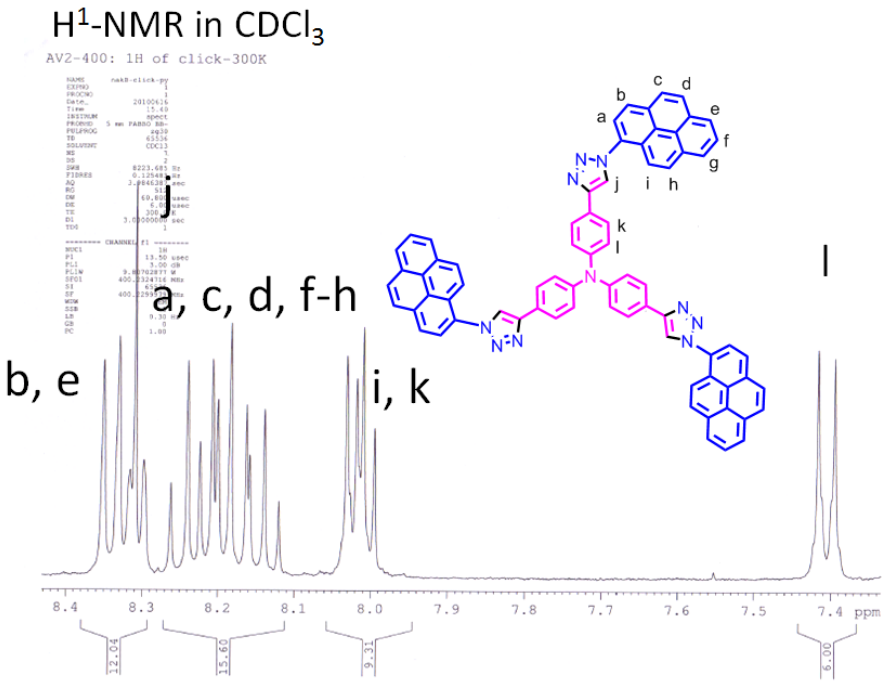


Fig. S4.10 ^{1}H-NMR (400 MHz) spectrum of **TAP**.

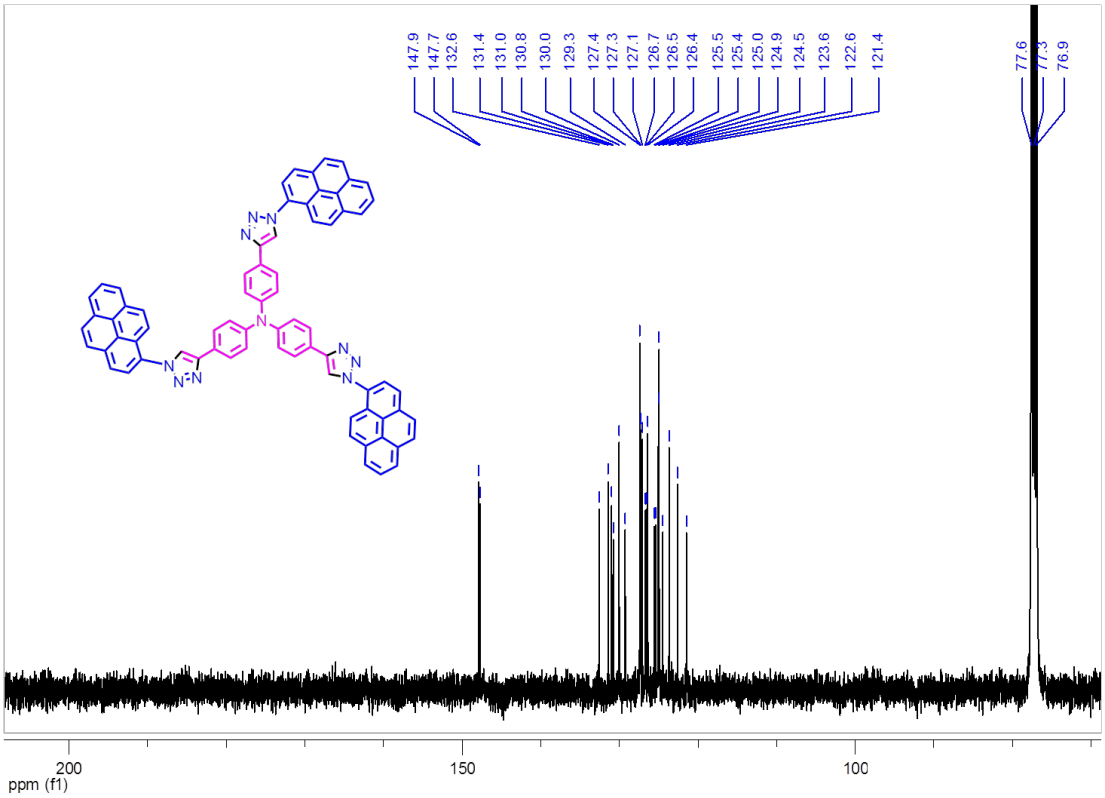


Fig. S4.11 ^{13}C-NMR (100 MHz) spectrum of **TAP**.

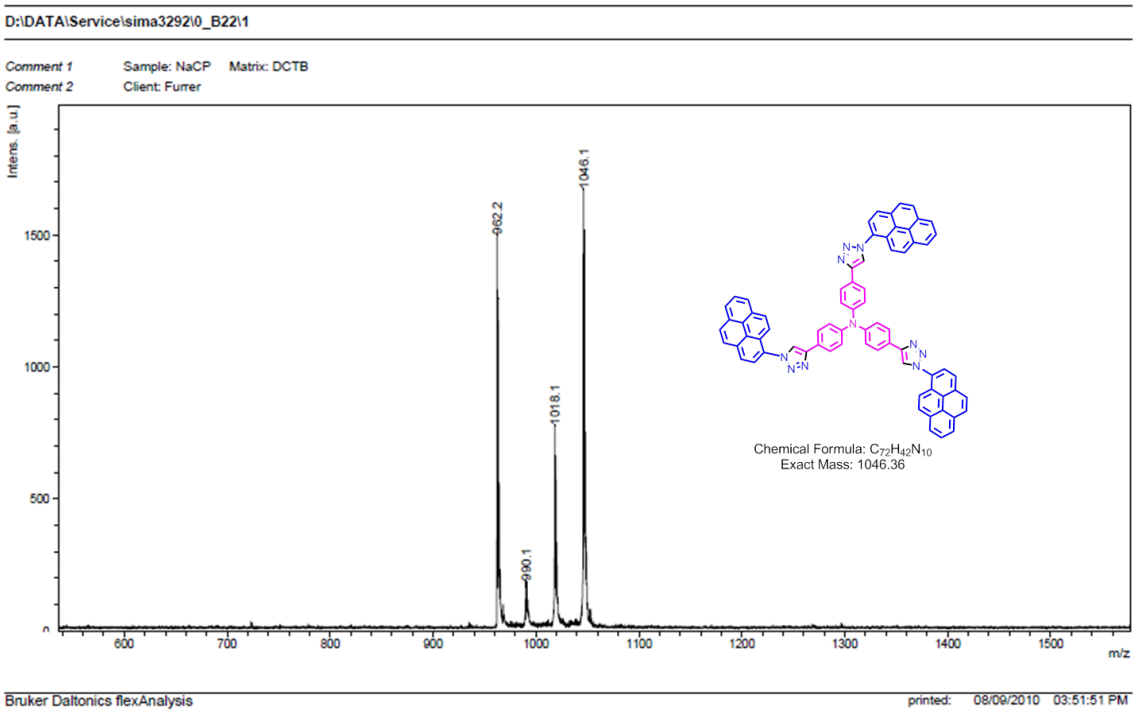


Fig. S4.12 MALDI-TOF-MS spectrum of **TAP**.

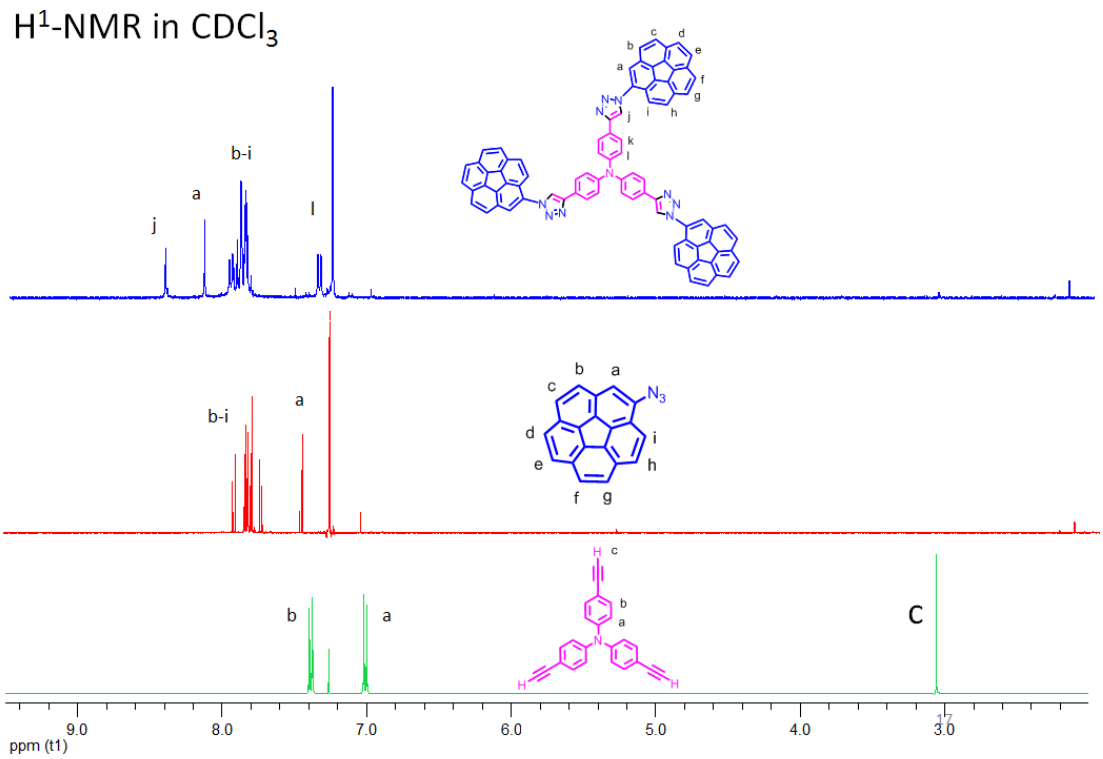


Fig. S4.13 Stacked plot of the ^{1}H-NMR (400 MHz) spectrum of **12**, **14**, and **TAC** in $CDCl_3$.

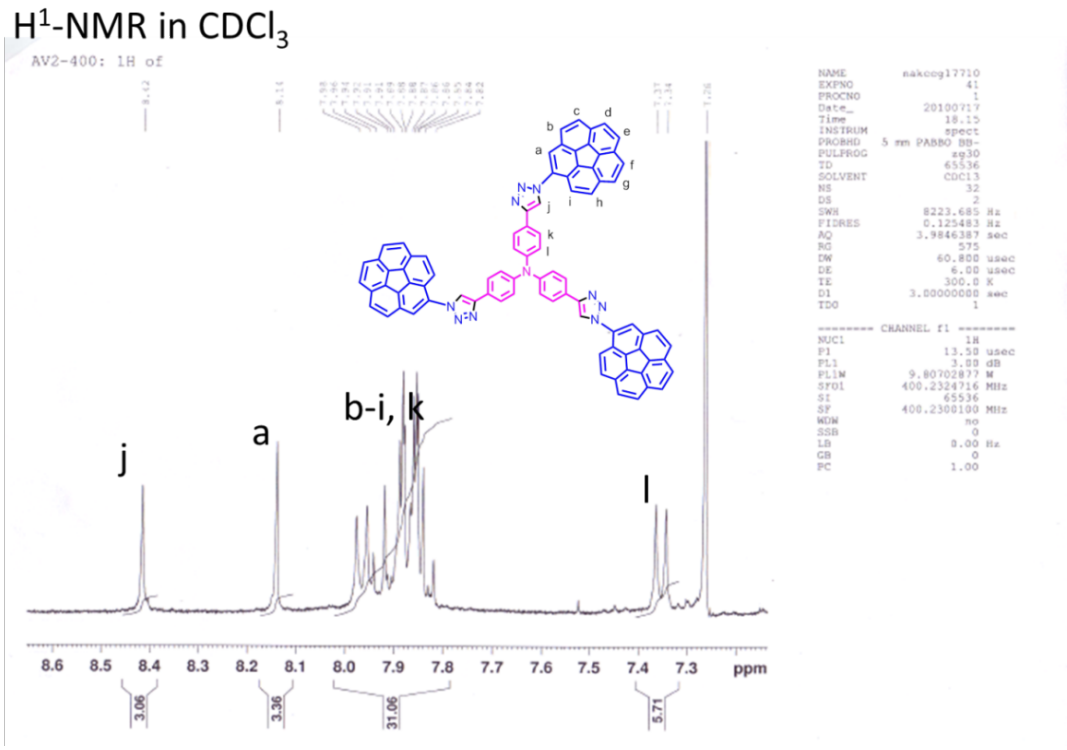


Fig. S4.14 ^{1}H-NMR (400 MHz) spectrum of **TAC**.

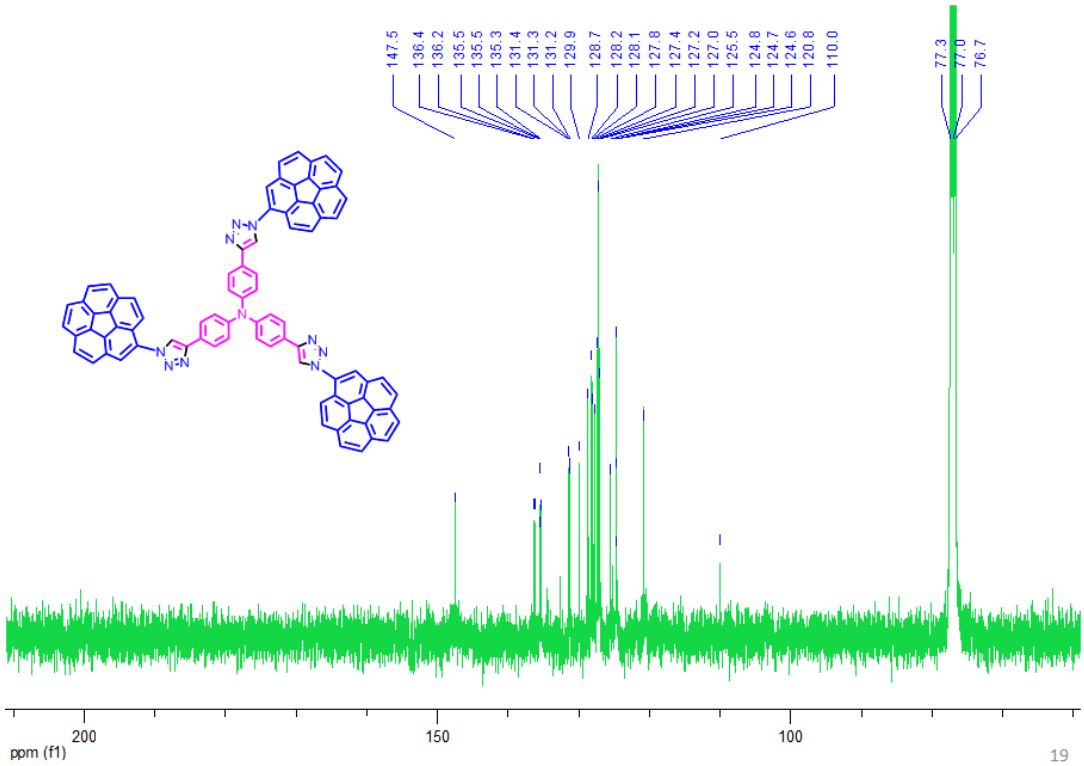


Fig. S4.15 ^{13}C-NMR (100 MHz) spectrum of **TAC**.

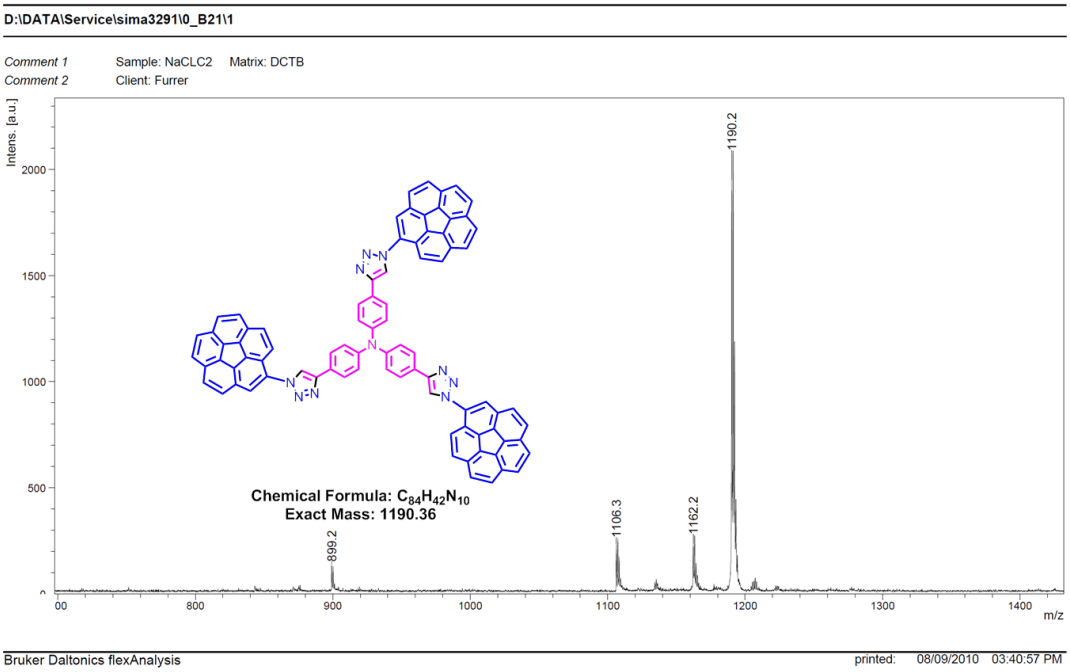


Fig. S4.16. MALDI-TOF-MS spectrum of **TAC**.

5. Photo physical properties of all fluorophores.

Table S5.1. Photo physical properties of TEP, TEC, TAP, and TAC.

compd	absorption		fluorescence	
	λ_{max}(nm)	ε (M^{-1} cm^{-1})	λ_{max}(nm)	Φ_F[a]
TEP	421	92775	484	0.24
TEC	415	58353	494	0.19
TAP	345	94342	506	0.046
TAC	329	57540	537	0.096

[a] Quinine sulfate in 0.1 M H_2SO_4 (Φ= 0.54) is the reference.

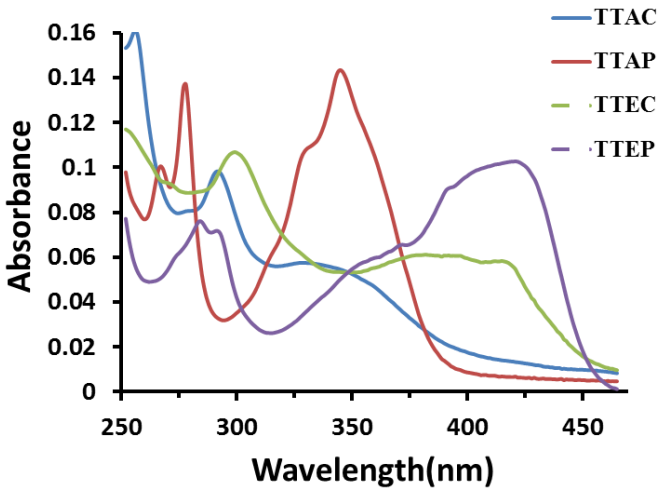


Fig. S5.1 Absorption spectra of TAC, TAP, TEC, and TEP (1 μM) in $CHCl_3$.

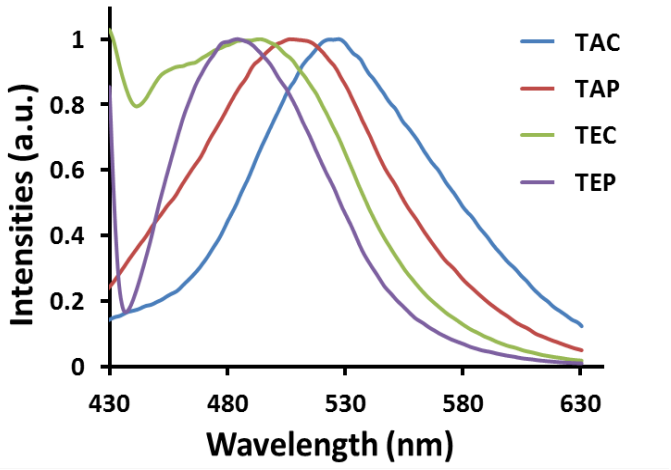


Fig. S5.2 The normalized fluorescent spectra of TAC, TAP, TEC, and TEP (1 μM) in $CHCl_3$ with the excitation wavelengths of 330, 345, 415, and 420 nm, respectively.

6. Computational Methodology

All calculations have been carried out using the GAMESS[1] and GAUSSIAN[2] software packages. The B97D density functional[3] was used together with the Def2-TZVPP basis set[4] for determination of structure and properties. An ultrafine grid was employed for all computations. A Hessian analysis (matrix of second derivative) was calculated for all structures, to determine local minima (positive definite) or nth-order saddle points (n negative eigenvalues), vibrational modes, and thermodynamic properties. Visualization and analysis of structural and property results were obtained using QMView[7] and WEBMO.[9] Depictions of highest occupied molecular orbitals are taken at isosurface value (MO) = 0.025, and isosurface value (ED) = 0.030.

[1]M. Schmidt, K. K. Baldridge, J. A. Boatz, S. Elbert, M. Gordon, J. H. Jenson, S. Koeski, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comp. Chem.*, 1993, **14**, 1347.
[2]Gaussian 09, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2009.
[3] S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.
[4]Rappoport, D.; Furche, F. *J. Chem. Phys.*, **2010**, *133*, 134105.
[8]Baldridge, K.K.; Greenberg, J. *J. Mol. Graph.*, **1995**, *13*, 63.
[9]WEBMO: http://www.webmo.net/index.html.

B97D/Def2-TZVPP

Molecule	E	E+ZPE	FF	Cation s.p.
tricorantriazolephenylamine (C3) TAC	-3772.1266594	-3771.124309	PD	-3771.91532303
tricornanynephenylamineB (C3) TEC	-3277.6430966	-3276.725448	PD	-3277.43536664
tripyrenetriazolephenylamine (C3) TAP	-3315.2092972	-3314.277975	PD	-3315.00281534
tripyreneyenphenylamine (C3) TEP	-2820.7244265	-2819.877724	PD	-2820.52540014
TNT	-884.8827366	-884.751830	PD	-884.528053356

B97D/Def2-TZVPP

Molecule	HOMO	HOMO (eV)	KT I.P.	ΔSCF I.P.	LUMO	LUMO (eV)
Tricorantriazolephenylamine (C3) TAC	-0.16206	-4.41	4.41	5.75	-0.10350	-2.82
tricornanynephenylamineB (C3) TEC	-0.16900	-4.60	4.60	5.65	-0.10356	-2.82
Tripyrenetriazolephenylamine (C3) TAP	-0.16005	-4.36	4.36	5.62	-0.09906	-2.70
Tripyreneyenphenylamine (C3) TEP	-0.16325	-4.44	4.44	5.42	-0.10050	-2.73
TNT (Cs)	-0.27119	-7.38	7.38	6.09	-0.15678	-4.27

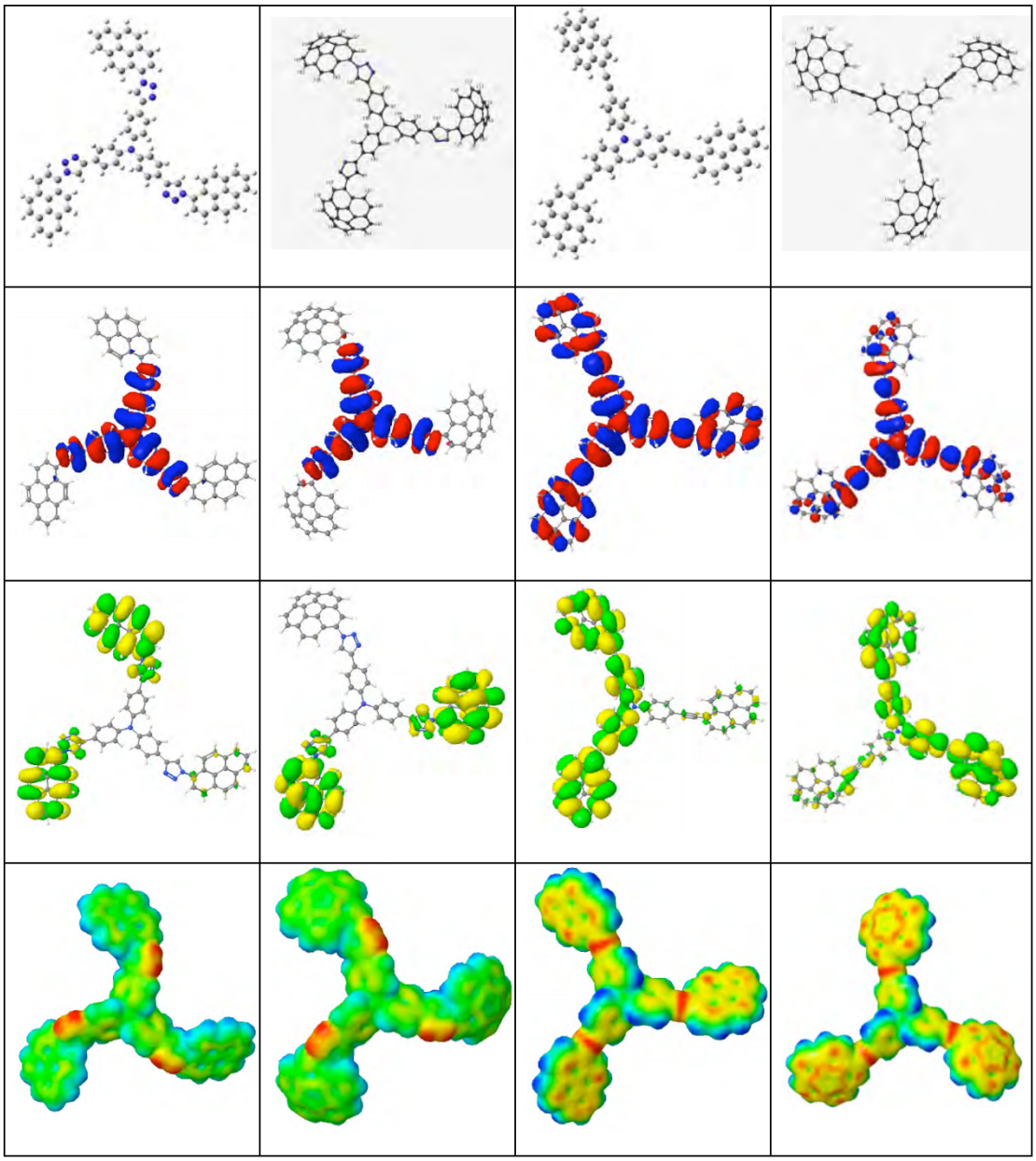


Figure S6.1. B97D/Def2-TZVPP calculated data, including HOMO images and MEP maps of fluorphores.

7. Study of ^{1}H-NMR and The K_{sv} plot at 5 °C, and 45 °C between TEP with TNT.

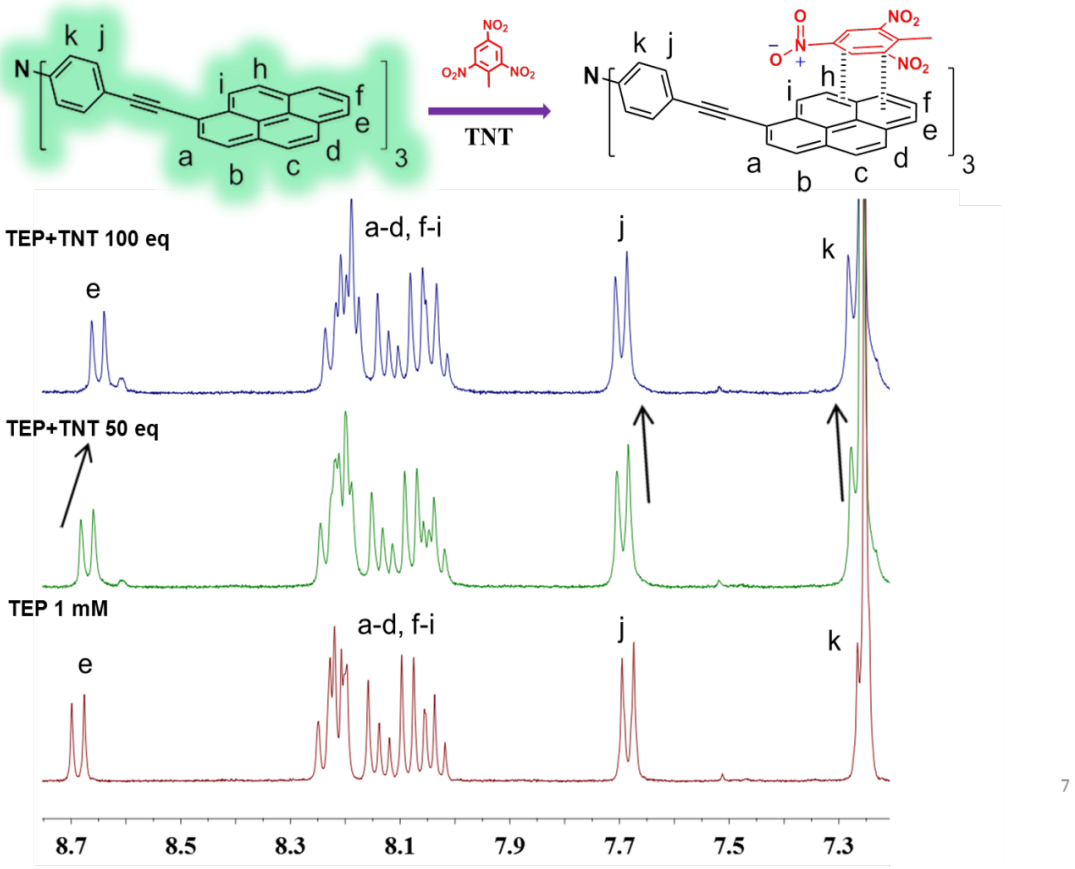


Fig. S7.1 Changes in the ^{1}H-NMR spectrum of TEP (1 mm) upon being subject to titration with increasing concentrations of TNT (0, 50, 100 equiv.) in $CDCl_3$.

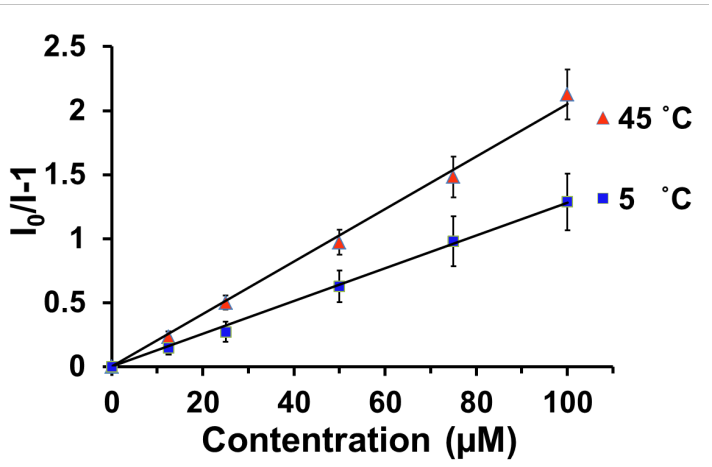


Fig. S7.2 The K_{sv} plot at 5 °C, and 45 °C showed which the K_{sv} value between TAP with TNT is increased from 13,565 ± 847 M^{-1}, and 19,650 ± 1597 M^{-1}, respectively. (Excited at 345 nm).

8. Structure of all analysts and PCA results from the fluorescent data.

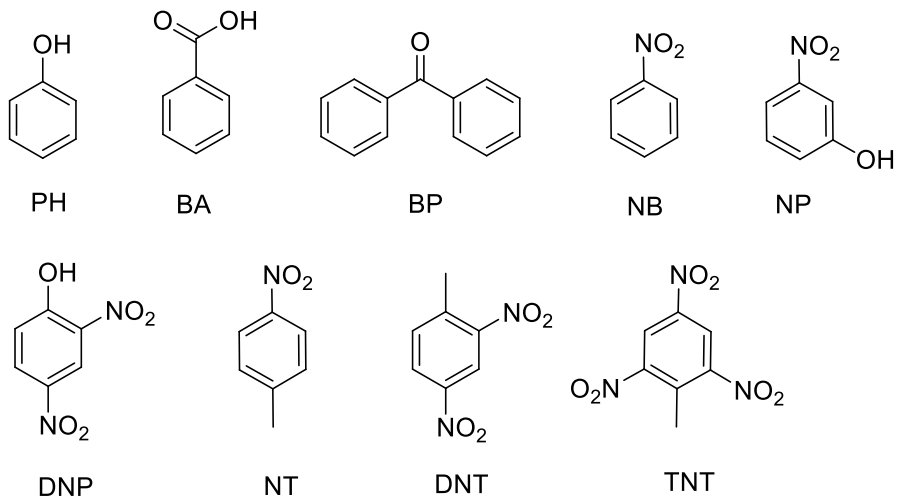


Fig. S8.1 The structure of the all analysts.

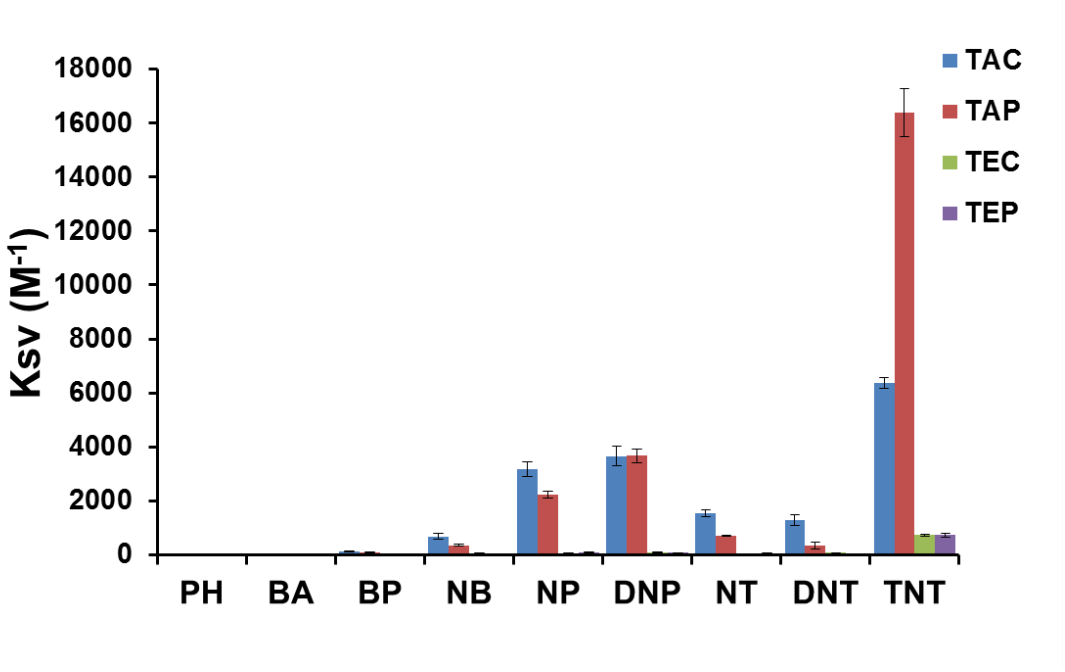
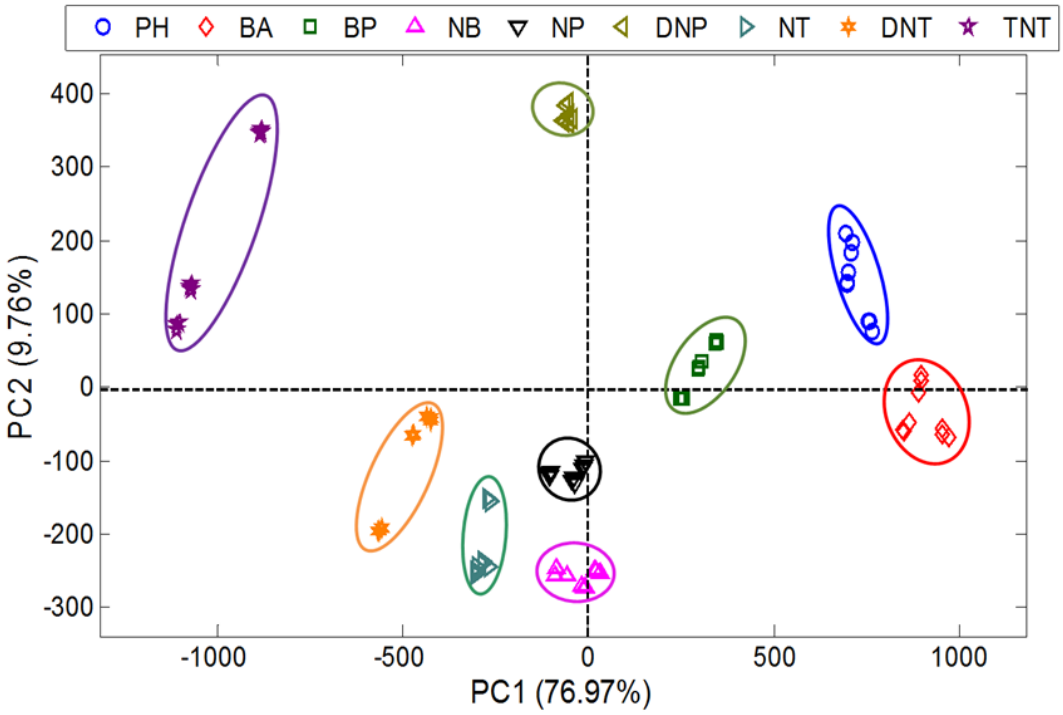


Fig. S8.2 Histogram plot of the K_{sv} values of nine aromatic compounds tested on four fluorophores in $CHCl_3$.



Classification accuracy = 96.30%

Fig. S8.3 Graphs of the first 2 PC scores including percent classification accuracy obtained from the fluorescence spectra using ΔI from all wavelengths (all flurophores).

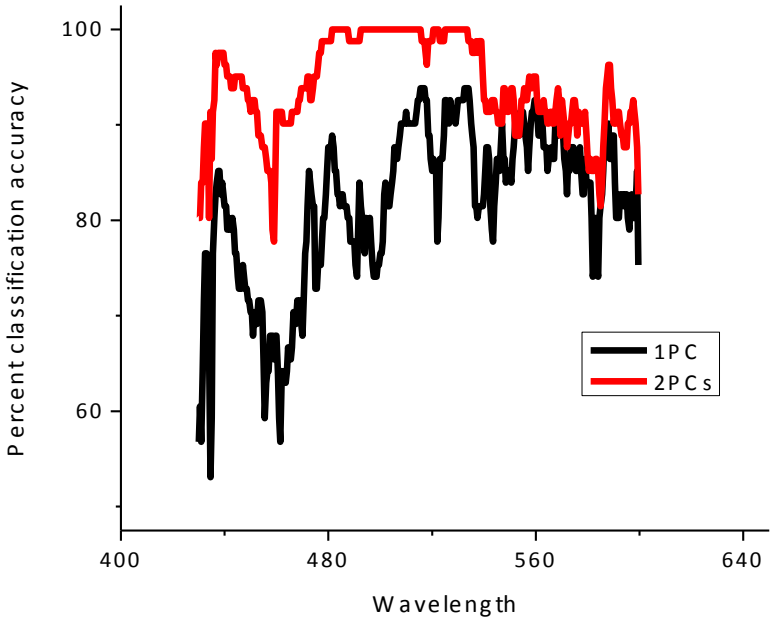


Fig. S8.4 The percent classification accuracy using LDA with leave one out cross-validation using ΔI measured at different wavelength.

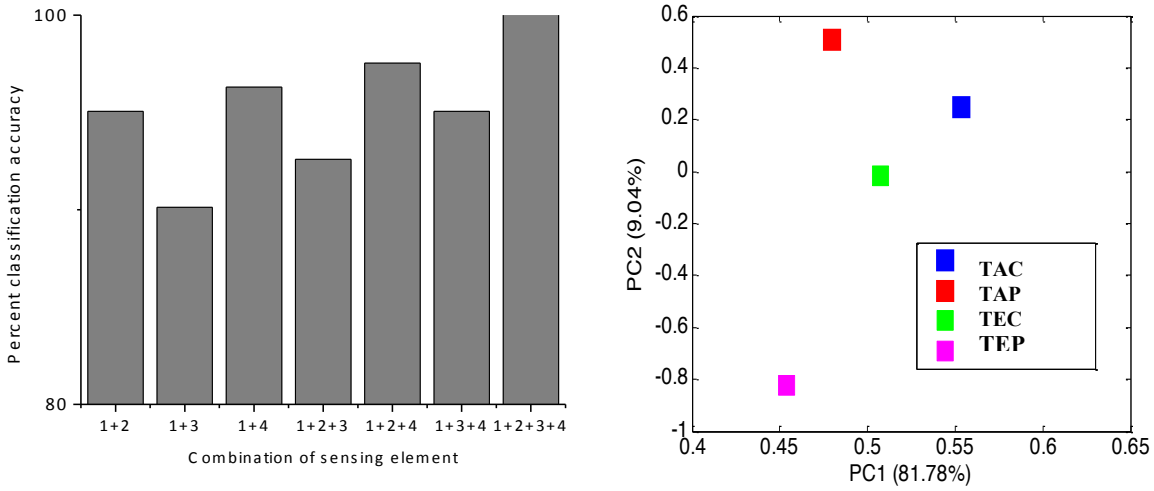


Fig. S8.5 (left) Percent classification accuracy using LDA with leave one out cross-validation calculated from each combination of sensing elements, (right) PC loading plot of ΔI measured at 500 nm.

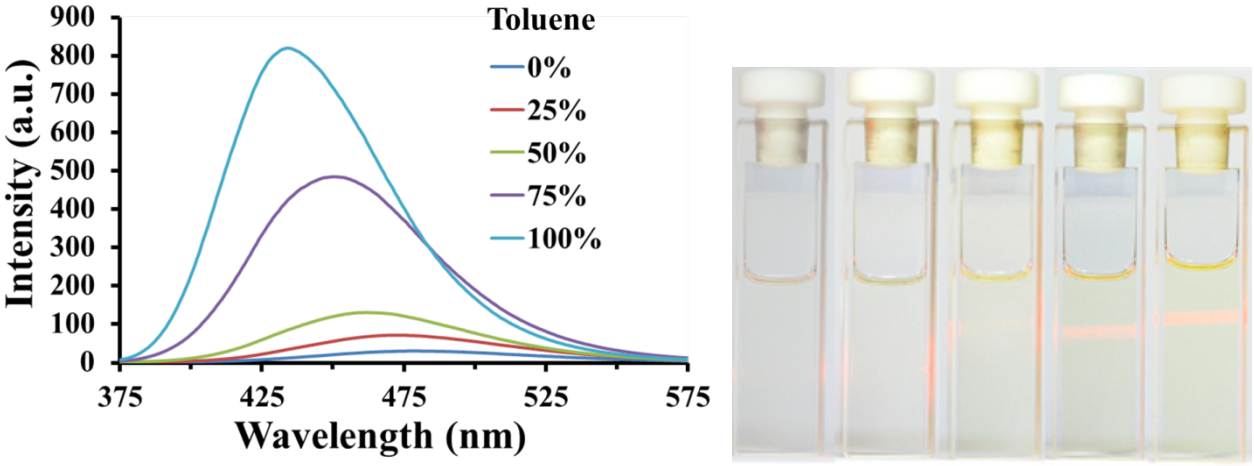


Fig. S8.6 The fluorescent spectra of TAP (0.2 μM) various toluene and $CHCl_3$.

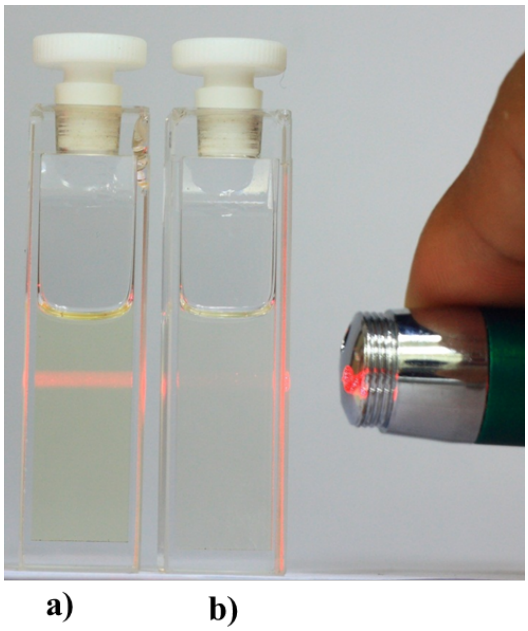


Fig. S8.7 Tyndall scattering of TAP solution a) $CHCl_3$/Toluene (1:3) (75%) and b) $CHCl_3$ with a laser light.

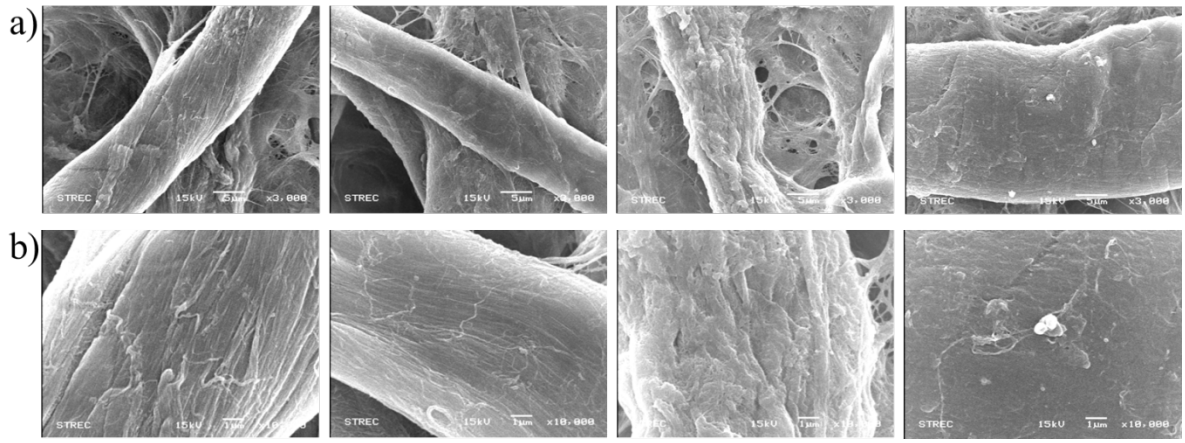


Fig. S8.8 SEM image of filters paper as cellulose fibers before as control and after spray solution of TAP in $CHCl_3$ to Toluene a) zoom as 3000x and b) zoom as 10,000x.