Supplementary Information for

Connecting Two Phenazines with a Four-Membered Ring:
Synthesis, Properties and Applications of Cyclobuta[1,2-b:3,4-b']diphenazines

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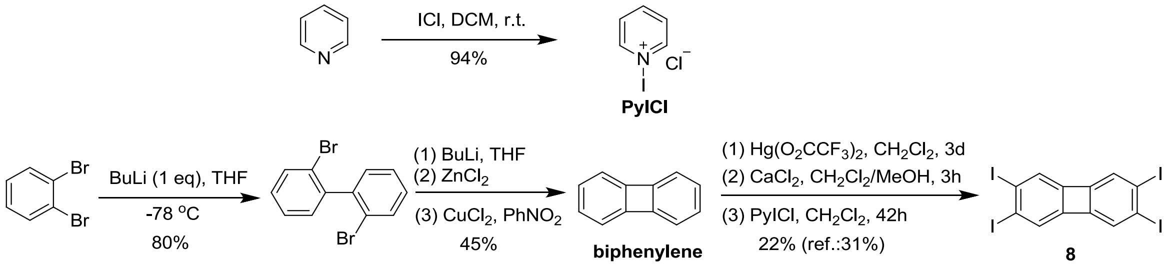
1. **Synthesis**

General: The reagents and starting materials employed were commercially available and used without any further purification if not specified elsewhere. Anhydrous and O_2-free diethyl ether, THF, CH_2Cl_2 and toluene were purified by an Advanced Technology Pure-Solv PS-MD-4 system. ^{1}H-NMR (400 MHz) or ^{13}C-NMR (100 MHz) spectra were recorded on a Brucker AVANCE III spectrometer. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (^{1}H-NMR, δ_H = 7.26 for $CDCl_3$; ^{13}C-NMR, δ_C = 77.16 for $CDCl_3$) as internal reference. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL spectrometer, Bruker 9.4T FTICR MS (solarix) spectrometer, or Bruker Autoflex speed MALDI-TOF MS spectrometer. Melting points were measured using a Nikon Polarizing Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage without calibration.



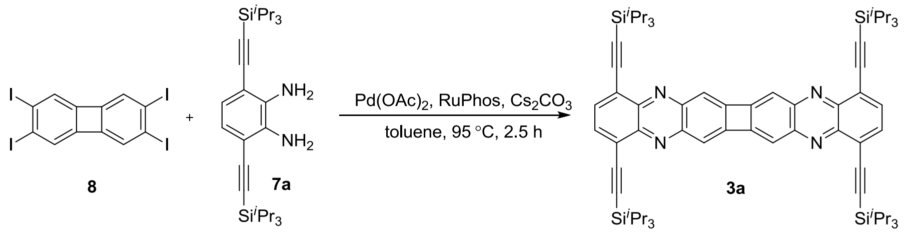
Monopyridineiodine (I) chloride (PyICl) was synthesis following the reported procedure [1] with minor modification. To a solution of pyridine (8.08 mL, 100 mmol, 1.05 eq) in 50 mL of dry CH_2Cl_2 was added a solution of ICl (5 mL, 95.5 mmol, 1 eq) in 200 mL of dry CH_2Cl_2 over 2 h at room temperature. After being stirred for another 1 h, the solvent was removed under reduced pressure to give a brown red solid. The solid was washed with ethanol to afford 21.7 g (89.9 mmol, 94%) of monopryridineiodine (I) chloride as a light yellow solid. PyICl: m.p.: 133-135°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, ^3J(H, H) = 4.8 Hz, 2H), 8.03 (t, ^3J(H, H) = 8.0 Hz, 1H), 7.48 (t, ^3J(H, H) = 6.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 140.2, 127.1 ppm.

Biphenylene was synthesized from 2,2'-dibromobiphenyl [2] following the reported procedures.[3]

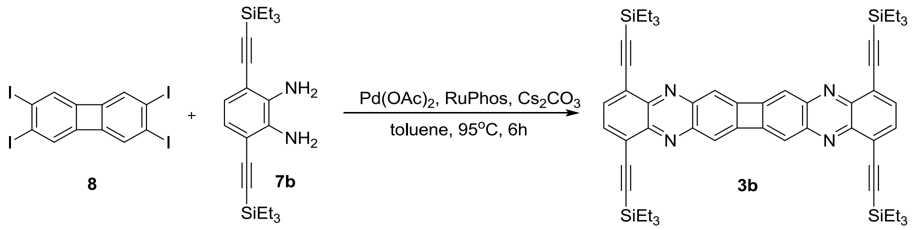
2,3,6,7-Tetraiodobiphenylene (8) was synthesized following the reported procedure [4] with modification as detailed below.
To a stirred of solution of $Hg(O_2CCF_3)_2$ (6.09 g, 14.3 mmol, 4.3 eq) in dry CH_2Cl_2 (100 mL) was added a solution of biphenylene (500 mg, 3.29 mmol, 1 eq) in 12 mL of CH_2Cl_2 at room temperature. The mixture was kept in dark and stirred at room temperature for 3 days. To the mixture was added a saturated solution of $CaCl_2$ (3.16 g, 28.5 mmol, 8.6 eq) in 25 mL of methanol, and the resultant mixture was stirred for another 3 h. The obtained light yellowish green slurry was filtered to afford yellowish green solid and the solid was washed with

1. G. B. Kauffman, K. L. Stevens, D. J. Royer, *Inorganic Syntheses*, **1963**, *7*, 176–180.
2. K. L. Chan, S. E. Watkins, C. S. K. Mak, M. J. McKiernan, C. R. Towns, S. I. Pascu, A. B. Holmes, *Chem. Commun.* **2005**, 5766–5768.
3. S. M. H. Kabir, M. Hasegawa, Y. Kuwatani, M. Yoshida, H. Matsuyama, M. Iyoda, *J. Chem. Soc., Perkin Trans. 1* **2001**, 159–165.
4. T. A. Albright, S. Oldenhof, O. A. Oloba, R. Padilla, K. P. C. Vollhardt, *Chem. Commun.* **2011**, *47*, 9039–9041.

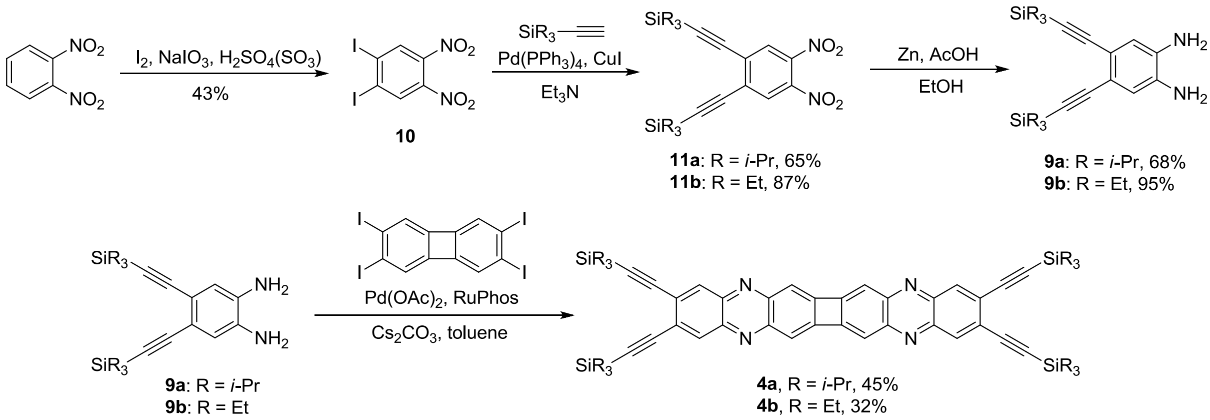
CH_2Cl_2 . Then the solid was suspended in dry CH_2Cl_2 (100 mL), and monopyridineiodine (I) chloride (9.51 g, 39.5 mmol, 12 eq) was added into this suspension. The color of mixture changed from yellow-green to dark brown, then quickly to orange. After being stirred at room temperature for another 42 h, the product was filtered off and the yellow solid washed with 1 M HCl (30 mL), H_2O (30 mL), MeOH (30 mL), acetone (50 mL) and CH_2Cl_2 (30 mL) successively to give 484 mg (0.74 mmol, 22%) of 2,3,6,7-tetraiodobiphenylene (**8**) as light yellow powder.
8: m.p.: >350 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (s, 4H) ppm; HRMS-EI$^+$ (*m/z*): calcd. for $C_{12}H_4I_4$ $[M]^+$ 655.6486; found, 655.6489.



A mixture of **8** (28 mg, 0.043 mmol, 1 eq), 3,6-bis((triisopropylsilyl)ethynyl)benzene-1,2-diamine (**7a**, 40 mg, 0.085 mmol, 2 eq), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol, 0.5 eq), RuPhos (10 mg, 0.021 mmol, 0.5 eq) and Cs_2CO_3 (82 mg, 0.25 mmol, 6 eq) in 4 ml of toluene was stirred at 95 ℃ for 2.5 h. After cooled to room temperature, the reaction mixture was filtered and the solid was washed with 20 mL of CH_2Cl_2. The resulting filtrate was concentrated under a reduced pressure and then purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/3, v/v) as eluent. After removal of solvent under a reduced pressure, the product was washed with acetone, yielding 15 mg (0.014 mmol, 33%) of **3a** as a orange solid.
3a: m.p.: >350°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 4H), 7.89 (s, 4H), 1.27 (s, 84H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.4, 147.2, 143.1, 134.0, 124.3, 121.2, 103.6, 100.9, 19.0, 11.6 ppm; HRMS (ESI$^+$): calcd. for $C_{68}H_{92}N_4Si_4$ $[M+H]^+$ 1077.6472; found, 1077.6462.



A mixture of **8** (28 mg, 0.043 mmol, 1 eq), 3,6-bis((triethylsilyl)ethynyl)benzene-1,2-diamine (**7b**, 32.8 mg, 0.085 mmol, 2 eq), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol, 0.5 eq), RuPhos (10 mg, 0.021 mmol, 0.5 eq) and Cs_2CO_3 (82 mg, 0.25 mmol, 6 eq) in 4 ml of toluene was stirred at 95 ℃ for 6 h. After being cooled to room temperature, the reaction mixture was filtered and the solid was washed with 20 mL of CH_2Cl_2. The resulting filtrate was concentrated under a reduced pressure, and then purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/2, v/v) as eluent, After removal of solvent under a reduced pressure, the product was washed with acetone, yielding 5.0 mg (0.0056 mmol, 13%) of **3b** as a orange solid.
3b: m.p.: >350°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 4H), 7.91 (s, 4H), 1.22 (t, ^3J(H, H) = 7.6 Hz, 36H), 0.85 (q, ^3J(H, H) = 8.0 Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 147.3, 142.9, 134.3, 124.1, 121.2, 102.8, 102.0, 7.8, 4.6 ppm; FTICR MS (*m/z*): calcd. for $C_{56}H_{68}N_4Si_4$ $[M+H]^+$ 909.4594; found, 909.4558.



4,5-Diiodo-1,2-dinitrobenzene (**10**) was synthesized following the reported procedure[5] with minor modification.

To stirred oleum (~20% free SO_3, 40 mL) were added I_2 (9.4 g, 37 mmol, 1.1 eq) and $NaIO_3$ (5.8 g, 29.3 mmol, 0.91 eq) in portions, and the resulting mixture was stirred for 10 min. Then 1,2-dinitrobenzene was added into the mixture slowly. When the addition was finished, the mixture was heated to100 ^{o}C and stirred for 12 h. When cooled to room temperature, the mixture was poured into ice-water and extracted with ethyl acetate (100 mL). The separated organic phase was washed with water and saturated $Na_2S_2O_3$ aqueous, and dried with anhydrous Na_2SO_4. After removing the solvent, the crude product was recrystallized from ethanol, gaving 5.88 g (14 mmol, 43%) of 4,5-diiodo-1,2-dinitrobenzene as a yellow solid.

10: m.p.: 188-189^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 2H) ppm. It was the same as that literature reaported.[6]

4,5-Di((triisopropylsilyl)ethynyl)-1,2-dinitrobenzene (11a)

To a suspension of 4,5-diiodo-1,2-dinitrobenzene (500 mg, 1.19 mmol, 1 eq), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol, 0.05 eq) and CuI (23 mg, 0.12 mmol, 0.1 eq) in dry Et_3N was add triisopropylsilylacetylene (800 μL, 3.57 mmol, 3 eq) under nitrogen at room temperature. The mixture was heated to 80 ^{o}C and stirred for 4 h. When cooled to room temperature, the mixture was extracted with ethyl acetate (30 mL) and washed with water and brine. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 /hexane (1/4, v/v) as eluent, yielding 410 mg (0.775 mmol, 68%) of **11a** as a light yellow solid.

11a: m.p.: 55–56 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 2H), 1.16-1.23 (m, 42H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 130.8, 129.7, 104.9, 101.7, 18.8, 11.3 ppm; HRMS-EI^{+} (*m/z*): calcd. for $C_{28}H_{44}N_2O_4Si_2$ $[M]^{+}$ 528.2834; found, 528.2844.

4,5-Di((triethylsilyl)ethynyl)-1,2-dinitrobenzene (11b)

To a suspension of 4,5-diiodo-1,2-dinitrobenzene (200 mg, 0.48 mmol, 1 eq), $Pd(PPh_3)_4$ (28 mg, 0.024 mmol, 0.05 eq) and CuI (9.1 mg, 0.048 mmol, 0.1 eq) in dry Et_3N was add triisethylsilylacetylene (256 μL, 1.43 mmol, 3 eq) under nitrogen at room temperature. The mixture was heated to 80 ^{o}C and stirred for 4 h. When cooled to room temperature, the

5. J. Wang, L. Wang, CN1887851, **2007**.
6. W. J. Youngblood, *J. Org. Chem.* **2006**, *71*, 3345–3356.

mixture was extracted with ethyl acetate (20 mL) and washed with water and brine. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using CH2Cl2 /hexane (1/3, v/v) as eluent, yielding 184 mg (0.414 mmol, 87%) of **11b** as a light yellow solid.
11b: m.p.: 91–93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 2H), 1.07 (t, ^3J(H, H) = 8.0 Hz, 12H), 0.75 (q, ^3J(H, H) = 8.0 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 131.1, 129.1, 105.6, 100.8, 7.6, 4.2 ppm; MALDI-TOF MS (*m/z*): calcd. for $C_{22}H_{32}N_2O_4Si_2$ $[M]^+$ 444.1895; found, 444.1893.

4,5-Bis((triisopropylsilyl)ethynyl)benzene-1,2-diamine (9a) was synthesized following the reported procedure [7] with minor modification.
To a solution of **11a** (200 mg, 0.38 mmol, 1 eq) in 25 mL of absolute ethanol and 2.5 mL of acetate acid was added zinc dust (544 mg, 8.32 mmol, 22 eq) in portions. After being stirred for 30 min, the reaction mixture was filtered to remove the excessive zinc dust. The filtrate was diluted with ethyl acetate (40 mL) and washed with water, saturated aqueous solution of $NaHCO_3$, and brine. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 /hexane (1/1, v/v) as eluent, yielding 121 mg (0.26 mmol, 68%) of **9a** as an off white solid.
9a: m.p.: 100–102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (s, 2H), 3.47 (bs, 4H), 1.12-1.10 (m, 42H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.1, 120.8, 117.7, 106.3, 91.6, 18.9, 11.5 ppm; HRMS-ESI$^+$ (*m/z*): calcd. for $C_{28}H_{48}N_2Si_2$ $[M+H]^+$ 469.3429; found, 469.3427.

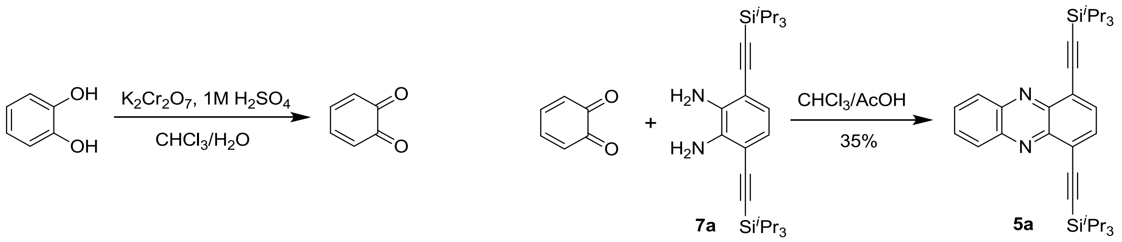
4,5-Bis((triethylsilyl)ethynyl)benzene-1,2-diamine (9b) was synthesized following the reported procedure [7] with minor modification.
To a solution of **11b** (184 mg, 0.414 mmol, 1 eq) in 25 mL of absolute ethanol and 2.5 mL of acetate acid was added zinc dust (596 mg, 9.11 mmol, 22 eq) in portions. After being stirred for 30 min, the reaction mixture was filtered to remove the excessive zinc dust. The filtrate was diluted with ethyl acetate (40 mL) and washed with water, saturated aqueous solution of $NaHCO_3$, and brine. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 /hexane (1/1, v/v) as eluent, yielding 151 mg (0.393 mmol, 95%) of **9b** as off white solid.
9b: m.p.: 56–58 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (s, 2H), 3.45 (bs, 4H), 1.06 (t, ^3J(H, H) = 8.0 Hz, 12H), 0.69 (q, ^3J(H, H) = 8.0 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.1, 120.4, 117.9, 105.4, 92.9, 7.77, 4.66 ppm; HRMS-ESI$^+$ (*m/z*): calcd. for $C_{22}H_{35}N_2Si_2$ $[M+H]^+$ 385.2490; found, 385.2484.

2,3,10,11-Tetra((triisopropylsilyl)ethynyl)cyclobuta[1,2-b:3,4-b']diphenazine (4a)
A mixture of **8** (28 mg, 0.043 mmol, 1 eq), 4,5-bis((triisopropylsilyl)ethynyl)benzene-1,2-diamine (**9a**, 40 mg, 0.085 mmol, 2 eq), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol, 0.5 eq), RuPhos (10 mg, 0.021 mmol, 0.5 eq) and Cs_2CO_3 (82 mg, 0.25 mmol, 6 eq) in 4 ml of toluene was stirred at 110 ℃ for 3 h. After cooled to room temperature, the reaction mixture was filtered and the solid was washed with 20 mL of CH_2Cl_2. The resulting filtrate was concentrated under a reduced pressure and then purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/3, v/v) as eluent, yielding 23.0 mg (0.019 mmol, 45%) of **4a** as a red solid.

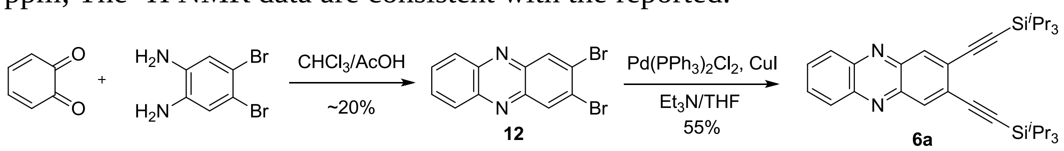
7. J. D. Spence, A. C. Rios, M. A. Frost, C. M. McCutcheon, C. D. Cox, S. Chavez, R. Fernandez, B. F. Gherman, *J. Org. Chem.* **2012**, *77*, 10329−10339.

4a: m.p. >350°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 4H), 7.86 (s, 4H), 1.18 (s, 84H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 147.7, 142.1, 134.6, 127.3, 120.9, 104.6, 99.3, 18.9, 11.5 ppm; HRMS-ESI$^+$ (*m/z*): calcd. for $C_{68}H_{92}N_4Si_4$ $[M+H]^+$ 1077.6472; found, 1077.6479.

2,3,10,11-Tetra((triethylsilyl)ethynyl)cyclobuta[1,2-b:3,4-b']diphenazine (**4b**)
A mixture of **8** (28 mg, 0.043 mmol, 1 eq), 4,5-bis((triethylsilyl)ethynyl)benzene-1,2-diamine (**9b**, 33 mg, 0.085 mmol, 2 eq), $Pd(OAc)_2$ (4.8 mg, 0.021 mmol, 0.5 eq), RuPhos (10 mg, 0.021 mmol, 0.5 eq) and Cs_2CO_3 (82 mg, 0.25 mmol, 6 eq) in 4 ml of toluene was stirred at 100 ℃ for 3 h. After cooled to room temperature, the reaction mixture was filtered and the solid was washed with 20 mL of CH_2Cl_2. The resulting filtrate was concentrated under a reduced pressure and then purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/3, v/v) as eluent, yielding 12.5 mg (0.014 mmol, 32%) of **4b** as a red solid.
4b: m.p.: >350 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 4H), 7.86 (s, 4H), 1.13 (t, ^3J(H, H) = 7.6 Hz, 36H), 0.78 (q, ^3J(H, H) = 7.6 Hz, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 147.7, 142.2, 134.1, 127.3, 120.9, 103.7, 100.1, 7.8, 4.5 ppm; HRMS (*m/z*): calcd. for $C_{56}H_{68}N_4Si_4$ $[M]^-$ 908.4516; found, 908.4531.



1,4-Di((triisopropylsilyl)ethynyl)phenazine (5a).
To a solution of $K_2Cr_2O_7$ (3.53 g, 12.00 mmol, 12 eq) in 70 mL of 1 M H_2SO_4 were added a solution of catechol (0.66 g, 6.00 mmol, 6 eq) in 140 mL of chloroform. The mixture was stirred at room temperature for 15 min. Then the organic layer was separated and washed with brine, dried over anhydrous Na_2SO_4. After removal of Na_2SO_4, the solution of crude 1,2-benzoquinone in chloroform was mixed with acetic acid (6 mL) and 1,4-di((triisopropylsilyl)ethynyl)phenylene-diamine (470 mg, 1mmol, 1eq). The resultant mixture was stirred at 45 °C overnight, and then concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/4, v/v) as eluent, yielding 190 mg (0.35 mmol, 35%) of **5a** as a yellow solid.
5a: m.p.: 96–98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (dd, ^3J(H, H) = 6.4 Hz, ^4J(H, H) = 3.2 Hz, 2H), 7.94 (s, 2H) 7.86 (dd, ^3J(H, H) = 6.8 Hz, ^4J(H, H) = 3.2 Hz, 2H), 1.27–1.25 (m, 42H) ppm; The ^{1}H NMR data are consistent with the reported.[8]



2,3-Dibromophenazine (12).
To a solution of $K_2Cr_2O_7$ (3.53 g, 12.00 mmol, 12 eq) in 70 mL of 1 M H_2SO_4 were added a solution of catechol (0.66 g, 6.00 mmol, 6 eq) in 140 mL of chloroform. The mixture was stirred at room temperature for 15 min. Then the organic layer was separated and washed

8. J. J. Bryant, Y. Zhang, B. D. Lindner, E. A. Davey, A. L. Appleton, X. Qian, U. H. F. Bunz, *J. Org. Chem.*, **2012**, *77*, 7479–7486.

with brine, dried over anhydrous Na_2SO_4. After removal of Na_2SO_4, the solution of crude 1,2-benzoquinone in chloroform was mixed with acetic acid (6 mL) and 2,3-dibromophenylenediamine (266 mg, 1mmol, 1eq). The resultant mixture was stirred at 45 ^oC overnight, and then concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/1, v/v) as eluent, yielding 68 mg (0.20 mmol, 20%) of **12** as a pale orange solid.

12: m.p.: 249–250 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 2H), 8.23 (dd, ^3J(H, H) = 6.8 Hz, ^4J(H, H) = 3.4 Hz, 2H), 7.90 (dd, ^3J(H, H) = 6.8 Hz, ^4J(H, H) = 3.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 142.4, 133.5, 131.6, 129.9, 127.7 ppm; MALDI-TOF HRMS (*m/z*): calcd. for $C_{12}H_6Br_2N_2$ $[M+H]^+$ 338.8950; found, 338.8942.

2,3-Di((triisopropylsilyl)ethynyl)phenazine (6a).

To a suspension of **12** (50 mg, 0.15 mmol, 1 eq), $Pd(PPh_3)_4$ (10.4 mg, 0.015 mmol, 0.1 eq) and CuI (2.8 mg, 0.015 mmol, 0.1 eq) in 2 mL of dry Et_3N and 2 mL of THF was added triisopropylsilylacetylene (134 μL, 0.60 mmol, 4 eq) under a nitrogen atmosphere at room temperature. The mixture was heated to 80 ^oC and stirred for 39 h. After cooled to room temperature, the mixture was extracted with ethyl acetate (10 mL) and washed with water and brine. The organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 /hexane (1/2, v/v) as eluent, yielding 44 mg (0.081 mmol, 55%) of **6a** as a yellow solid.

6a: m.p.: 166–168 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 2H), 8.21 (dd, ^3J(H, H) = 6.8 Hz, ^4J(H, H) = 3.6 Hz, 2H), 7.85 (dd, ^3J(H, H) = 6.4 Hz, ^4J(H, H) = 3.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 142.7, 134.9, 131.2, 129.9, 127.0, 104.7, 99.1 ppm; MALDI-TOF HRMS (*m/z*): calcd. for $C_{344}H_{48}N_2Si_2$ $[M]^-$ 540.3356; found, 540.3337.

2. Stability test

Differential scanning calorimetry (DSC) thermograms were measured on a Mettler Toledo DSC3 STAR system. ^1H-NMR (400 MHz) spectra were recorded on a Brucker AVANCE III spectrometer, using residual solvent protons (^1H-NMR, δ_H = 7.26 for $CDCl_3$) as internal reference. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 Plus UV-VIS-NIR spectrophotometer.

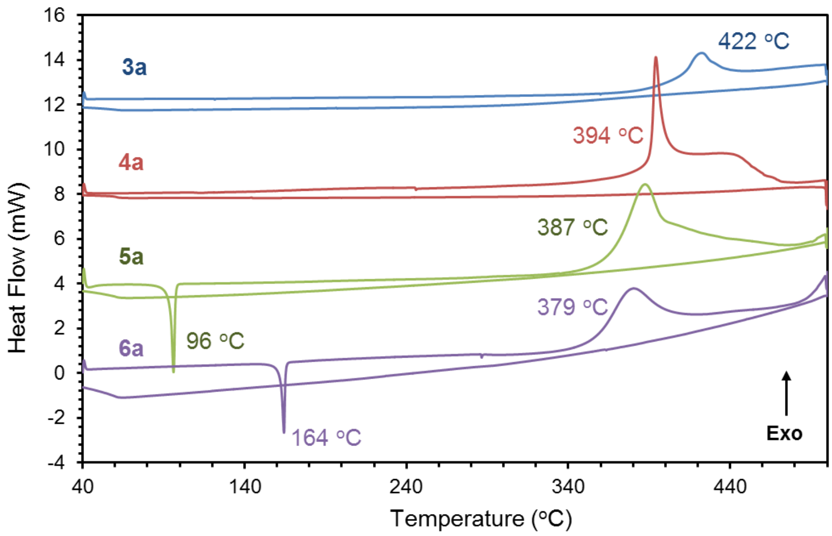


Figure S1. DSC thermograms of heating and cooling for **3a**, **4a**, **5a** and **6a**. The heating rate used for heating and cooling of all samples was 10 ℃ min^{-1}.

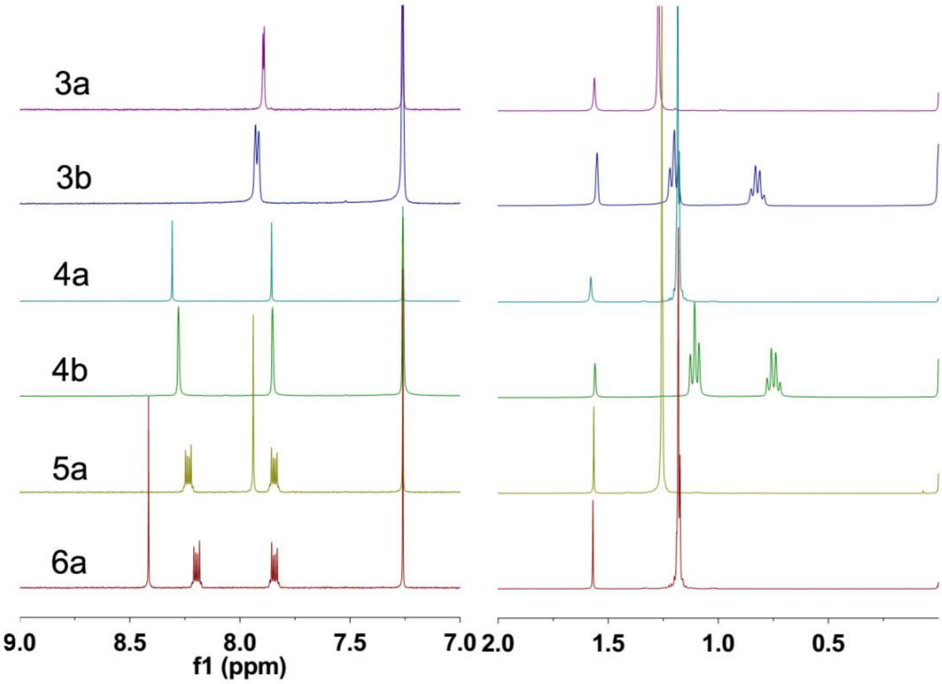


Figure S2. Partial ^{1}H-NMR spectra of **3a-b**, **4a-b**, **5a** and **6a** in $CDCl_3$. All samples were heated at 200 ℃ for 4 h in air before dissolved in $CDCl_3$ for test with ^{1}H-NMR.

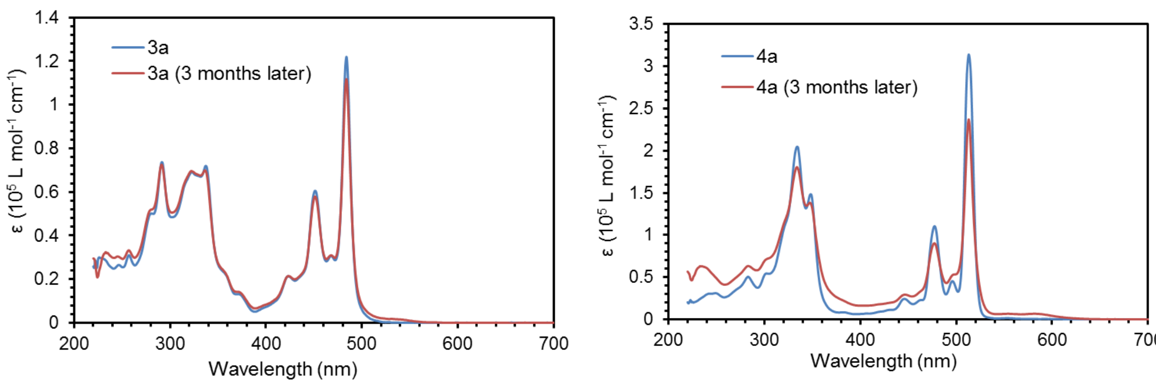


Figure S3. Absorption spectra of 0.01 mM solutions of **3a** and **4a** before (blue) and after (red) being stored for 3 months under ambient condition (14 h in light and 10 h in dark per day at room temperature).

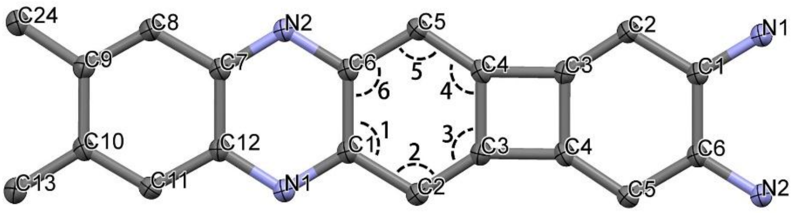
3. Single crystal structures

X-ray crystallography data were collected on a Bruker AXS Kappa ApexII Duo Diffractometer or Bruker D8 Venture Diffractometer. The single crystals of **3b** were grown from a solution in mixed solvents of CH_2Cl_2/ethyl acetate (v/v, 2:1) by slow evaporation of solvents. The single crystals of **4a** were grown from a solution of **4a** in mixed solvents of CH_2Cl_2/acetone (v/v, 3:1) by slow evaporation of solvents. The single crystals of **6a** were grown from a solution of **6a** in mixed solvents of CH_2Cl_2/ethyl acetate (v/v, 1:1) by slow evaporation of solvents.

Table S1. Crystallographic data of **3b**, **4a** and **6a**.

		3b	4a	6a
Empirical Formula		$C_{56}H_{68}N_4Si_4$	$C_{68}H_{92}N_4Si_4$	$C_{34}H_{48}N_2Si_2$
Space Group		P$\bar{1}$	P$\bar{1}$	P2$_1$/n
Temperature (K)		296(2)	296(2)	302(2)
Crystal system		Triclinic	Triclinic	Monoclinic
Unit Cell Lengths (Å)	*a*	7.19	11.30	7.70
	b	13.24	12.86	38.40
	c	15.09	13.68	11.92
Unit Cell angles (°)	*α*	74.08	66.85	90.00
	β	85.47	71.17	100.98
	γ	85.63	70.62	90.00
Cell Volume (Å^3)		1375.04 (16)	1682.21(15)	3460.3(4)
Z		1	1	4
Final R indices [I>2σ(I)]	R_1	0.0819	0.0720	0.0778
	wR_2	0.2116	0.1997	0.2028

Table S2. Analysis of bond angle in the carbon ring (C1-C6) in **3b**, **4a**, **5a** and **6a**.[a]



	3b	4a	5a	6a
∠**1**	120.36	120.57	119.09/118.55	118.64
∠**2**	115.70	116.05	121.06/120.72	119.59
∠**3**	123.46	123.27	119.68/121.01	121.62
∠**4**	123.53	123.21	120.92/120.81	121.49
∠**5**	115.76	115.90	121.04/119.09	119.66
∠**6**	121.18	120.86	118.06/119.80	118.98

[a]Bond angles were calculated from single crystal structures.

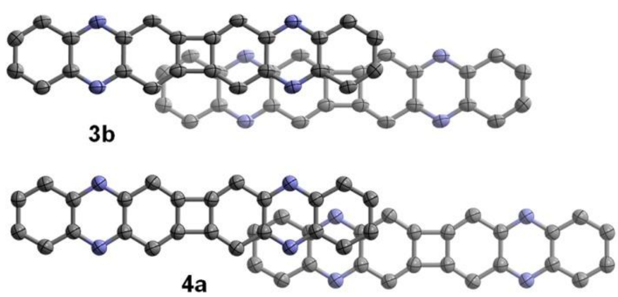


Figure S4. Crystal structures of **3b** and **4a** showing π-overlap (C and N atoms in the polycyclic backbone are shown as ellipsoids at the 50% probability level; the substituents and hydrogen atoms are removed).

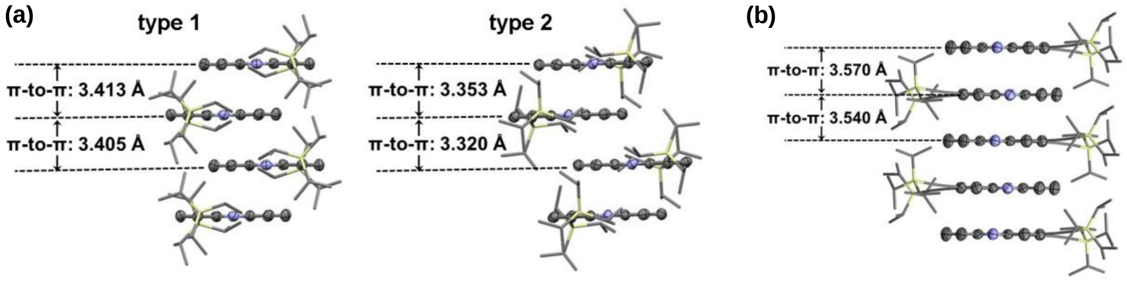


Figure S5. One dimensional π-stacked columns of **5a** (a) and **6a** (b) with π-π distance labeled. C and N atoms in the polycyclic backbone are shown as ellipsoids at the 50% probability level; the substituent groups are shown as sticks. Hydrogen atoms are removed for clarity.

4. Cyclic voltammetry

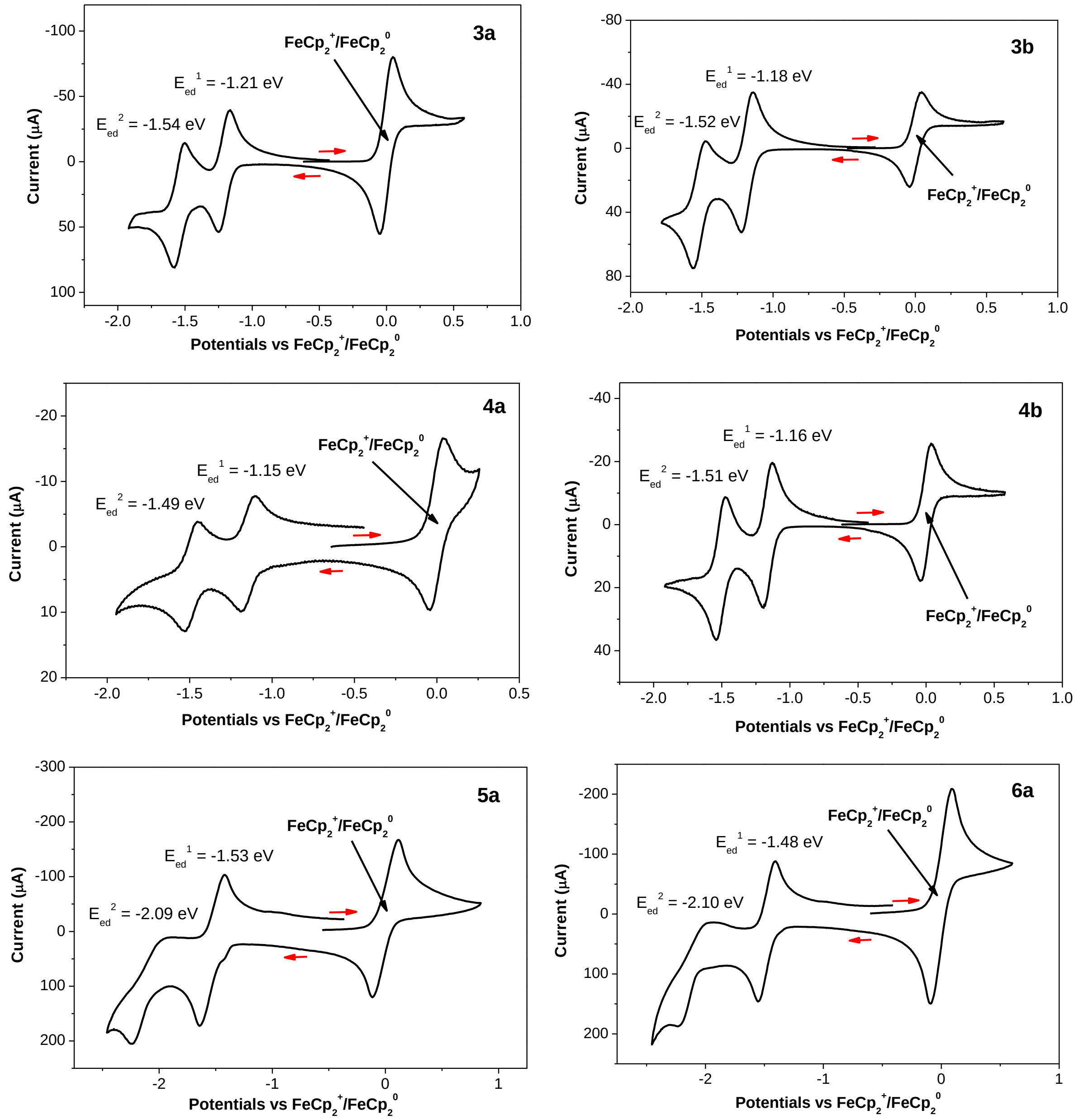


Figure S6. Cyclic voltammograms of **3a-b**, **4a-b**, **5a** and **6a** recorded in CH_2Cl_2 with $FeCp_2^+/FeCp_2^0$ as the internal standard.

Cyclic voltammetry was performed on a PAR Potentiostat/Galvanostat Model 263A Electrochemical Station (Princeton Applied Research) at a scan rate of 50 mVs^{-1}. All compounds were dissolved in anhydrous CH_2Cl_2 that contained 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. A platinum bead was used as a working electrode, a platinum wire was used as an auxiliary electrode, and a silver wire was used as a pseudo-reference. Ferrocenium/ferrocene was used as an internal standard.

5. UV-vis absorption and emission spectra

UV-vis absorption spectra were recorded on a Shimadzu UV-3600 Plus UV-VIS-NIR spectrophotometer. Fluorescence spectra were taken on a Hitachi F-7000 fluorescence spectrometer.

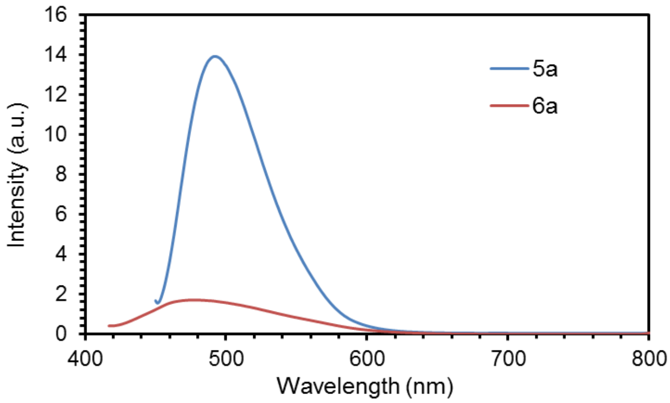


Figure S7. Emission spectra of **5a** and **6a** in CH_2Cl_2 (0.01 mM) when excited at 442 nm and 419 nm, respectively, and measured under the same condition. (The excitation wavelengths correspond to the maximum absorption wavelengths.)

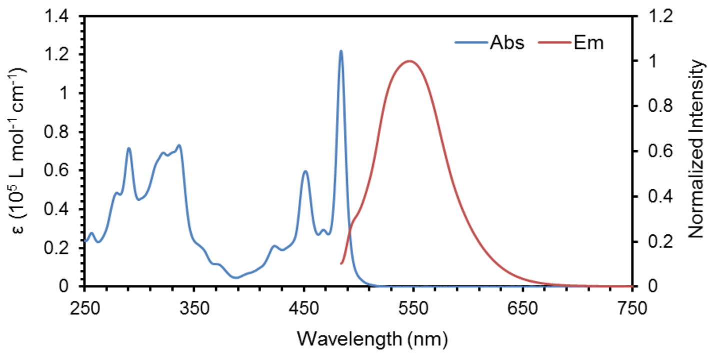


Figure S8. Absorption spectrum (blue line) and emission spectrum (red line) of **3b** in CH_2Cl_2 (0.01 mM) at room temperature. (The excitation wavelength of 484 nm corresponds to the maximum absorption wavelength.)

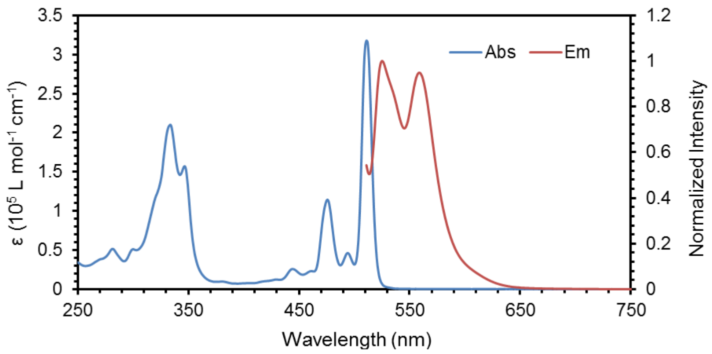


Figure S9. Absorption spectrum (blue line) and emission spectrum (red line) of **4b** in CH_2Cl_2 (0.01 mM) at room temperature. (The excitation wavelength of 511 nm corresponds to the maximum absorption wavelength.)

Quantum yields

The fluorescence quantum yields (Φ) of **3a-b**, **4a-b**, **5a** and **6a** were determined by comparing the photoluminescence integrated intensities and absorbance intensities with a standard, fluorescein (Φ = 0.925) [9] or perylene (Φ = 0.920).[10] The quantum yields were the calculated by using the following equation:[11]

$$\emptyset_s = \left(\frac{F_s}{F_r}\right)\left(\frac{A_r}{A_s}\right)\left(\frac{\eta_s}{\eta_r}\right)^2 \emptyset_r$$

Where F is the integrated intensities (area under emission peak), A is the absorbance, η is the refractive index and Φ is the quantum yield, the subscript s and r refer to sample and reference, respectively.
Fluorescein was dissolved in 0.1 M NaOH (η = 1.33), perylene was dissolved in ethanol (η = 1.36), and the samples (**3a-b**, **4a-b**, **5a** and **6a**) were dissolved in CH_2Cl_2 (η = 1.42). Absorbance values were kept below 0.05 at the excitation wavelength in order to minimize re-absorption effects.

Table S3. Relative fluorescence quantum yields.

Sample	Integrated intensities (F)	Absorbance at 470 nm (A)	Refractive index (η)	Quantum yield (Φ)
Fluorescein	358083	0.013	1.33	0.93
3a	23141	0.031	1.42	0.029
3b	27588	0.025	1.42	0.042
4a	136166	0.011	1.42	0.47
4b	77754	0.005	1.42	0.60
Sample	Integrated intensities (F)	Absorbance intensity at 400 nm (A)	Refractive index (η)	Quantum yield (Φ)
perylene	24394	0.032	1.36	0.92
5a	196	0.014	1.42	0.018
6a	40	0.022	1.42	0.0024

9. D. Magde, R. Wong, P. G. Seybold, *Photochem. Photobiol.* **2002**, *75*, 327–334.
10. J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024.
11. A. M. Brouwer, *Pure Appl. Chem.* **2011**, *83*, 2213–2228.

6. DFT calculations and analysis of molecular orbitals

To better understand the different photophysical properties of **3a** and **4a**, the frontier molecular orbitals of **3a**–**6a** were calculated using simplified model molecules **3a'**–**6a'**, which have smaller trimethylsilyl (TMS) groups replacing the TIPS groups to reduce computation cost. All the calculation were conducted using the Gaussian 09W software package.[12] The geometries of these simplified molecules were optimized at the B3LYP level of DFT with the 6-31G(d,p) basis set, and the molecular orbitals were then calculated with the 6-311++G(d, p) basis set. Excitation energies and oscillator strengths for the optimized structures were calculated with the TD-DFT method at the B3LYP/6-31G(d,p) level. The NICS values were obtained with the GIAO method at the B3LYP/6-311+G(d,p) level.

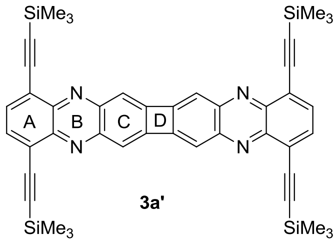
Table S4. Selected excitation energies and oscillator strengths of **3a'**, **4a'**, **5a'** and **6a'** calculated by the TD-DFT method.

	State	Excitation energy		Oscillator strength (*f*)	Excitation	Weight
		[eV]	[nm]			
3a'	1	2.2506	550.90	0.0000	HOMO → LUMO	0.70288
	2	2.3484	527.94	0.1425	HOMO-1 → LUMO	0.70231
	3	2.8087	441.42	0.9613	HOMO-3 → LUMO+2 HOMO-2 → LUMO HOMO → LUMO+2	-0.10806 0.66945 0.18340
	4	2.8892	429.12	0.0020	HOMO-5 → LUMO+1 HOMO-4 → LUMO	0.20747 0.66921
	5	2.9138	425.50	0.0000	HOMO-5 → LUMO HOMO-4 → LUMO+1	0.66510 0.21862
4a'	1	2.5129	493.39	1.7437	HOMO → LUMO HOMO-1 → LUMO+2	0.68564 0.14611
	2	2.5241	491.21	0.0074	HOMO-1 → LUMO	0.70244
	3	2.7734	447.05	0.0007	HOMO-2 → LUMO	0.70265
	4	2.8931	428.55	0.0020	HOMO-5 → LUMO+1 HOMO-4 → LUMO	0.20727 0.67292
	5	2.9162	425.15	0.0000	HOMO-5 → LUMO HOMO-4 → LUMO+1	0.66950 0.21699
5a'	1	2.6401	469.63	0.2163	HOMO → LUMO	0.69788
	2	2.9851	415.34	0.0014	HOMO-1 → LUMO	0.70077
	3	3.5059	353.64	0.0001	HOMO-2 → LUMO HOMO → LUMO+1	0.69236 -0.10469
	4	3.5816	346.17	0.0000	HOMO-4 → LUMO	0.69776
	5	3.6238	342.13	0.0001	HOMO-3 → LUMO	0.69665

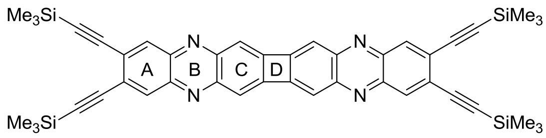
12. Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. 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, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

6a’	1	2.9458	420.89	0.0058	HOMO → LUMO	0.70142
	2	2.9993	413.38	0.0014	HOMO-2 → LUMO	0.70378
	3	3.1894	388.73	0.2678	HOMO-1 → LUMO HOMO → LUMO+1	0.64948 0.27467
	4	3.7653	329.28	0.0002	HOMO → 4 - LUMO	0.69631
	5	3.7732	328.59	0.0101	HOMO-3 → LUMO	0.69608

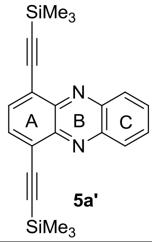
Table S5. NICS calculations for **3a’**, **4a’**, **5a’** and **6a’**.



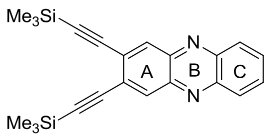
3a'



4a'



5a'



6a'

	3a’		**4a’**		**5a’**		**6a’**	
	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)
A	-6.59	-8.47	-7.02	-8.82	-6.86	-8.80	-7.48	-9.17
B	-6.99	-10.75	-6.01	-9.87	-9.41	-12.87	-8.33	-11.96
C	-3.05	-5.40	-2.95	-5.21	-7.22	-9.84	-7.01	-9.64
D	12.80	4.14	12.47	3.22				

Table S6. Cartesian coordinates (Å) for optimized structure of **3a’**, **4a’**, **5a’** and **6a’**.

3a’

atom	x	y	z
C	0.74355	0.72855	0.000437
C	0.7434	-0.72882	-0.000297
C	-0.74289	-0.72866	-0.000284
C	-0.74273	0.72871	0.000470
C	1.8795	1.47049	0.000786
C	3.11795	0.72915	0.000447
C	3.11785	-0.72999	-0.000498
C	1.8792	-1.471	-0.000835
C	-1.87885	-1.47062	-0.000837
C	-3.1173	-0.72928	-0.000504
C	-3.11713	0.72986	0.000589
C	-1.87852	1.47093	0.000909
N	-4.26342	-1.41274	-0.001161
C	-5.41439	-0.71919	-0.000527
C	-5.41422	0.7203	0.000738
N	-4.2631	1.41358	0.001281
C	-6.66625	-1.43577	-0.000922
C	-7.84585	-0.70354	-0.000119
C	-7.84568	0.7052	0.000952
C	-6.66592	1.43717	0.001337
N	4.26404	1.41266	0.000974
C	5.41503	0.71917	0.000484
C	5.41494	-0.72034	-0.000431

4a’

atom	x	y	z
C	-0.728195	0.731900	0.020797
C	-0.728779	-0.725294	0.018572
C	0.756786	-0.725943	0.017763
C	0.757415	0.731287	0.019861
C	-1.864355	1.473712	0.021772
C	-3.104949	0.736223	0.019955
C	-3.105487	-0.727699	0.017492
C	-1.865517	-1.466189	0.017102
C	1.892859	-1.467818	0.015259
C	3.133531	-0.730427	0.014357
C	3.134185	0.733594	0.016190
C	1.894175	1.472123	0.019254
N	4.276281	-1.421152	0.011327
C	5.426823	-0.718653	0.009536
C	5.427469	0.719724	0.011023
N	4.277569	1.423273	0.014588
C	6.666408	-1.409505	0.005755
C	7.869595	-0.728018	0.002846
C	7.870246	0.726866	0.003825
C	6.667680	1.409444	0.008109
N	-4.247842	1.426839	0.019900
C	-5.398362	0.724425	0.016818
C	-5.398826	-0.714097	0.014162

N	4.26384	-1.41369	-0.000997
C	6.66682	1.43586	0.000766
C	7.84649	0.70374	0.000422
C	7.84644	-0.70499	-0.000171
C	6.66673	-1.43705	-0.000578
C	6.6894	2.85719	0.000955
C	6.68931	-2.85835	-0.000585
C	-6.6883	2.8585	0.001853
C	-6.68895	-2.8571	-0.001639
C	6.74798	4.07716	0.000443
C	-6.74672	4.07847	0.001653
C	-6.74765	-4.07706	-0.001714
C	6.7479	-4.07831	0.000134
Si	-6.79535	-5.91753	-0.000745
C	-5.08903	-6.5629	0.486157
C	-7.25271	-6.51159	-1.735084
C	-8.0947	-6.4893	1.246076
Si	-6.79385	5.91896	0.000559
C	-8.09259	6.49103	-1.246760
C	-7.25153	6.51333	1.734698
C	-5.08716	6.5637	-0.485901
Si	6.79323	-5.91883	0.001499
C	5.31337	-6.55666	0.985899
C	6.70255	-6.52711	-1.784779
C	8.40762	-6.48481	0.803438
Si	6.79552	5.91763	-0.001703
C	8.09458	6.48873	-1.249137
C	7.2532	6.5128	1.732170
C	5.08904	6.56254	-0.488667
H	1.92477	2.55387	0.001124
H	1.92413	-2.55439	-0.001279
H	-1.92411	-2.554	-0.001306
H	-1.92352	2.55432	0.001283
H	-8.79177	-1.23423	-0.000272
H	-8.79149	1.23611	0.001428
H	8.79237	1.23452	0.000579
H	8.79226	-1.23586	-0.000208
H	-4.80598	-6.21685	1.485244
H	-5.07418	-7.65873	0.492330
H	-4.32244	-6.21962	-0.215641
H	-8.23517	-6.13537	-2.037581
H	-7.28661	-7.60643	-1.772222
H	-6.52211	-6.17303	-2.476489
H	-7.8577	-6.13962	2.255904
H	-9.08893	-6.11195	0.986147
H	-8.14883	-7.58354	1.274320
H	-8.14643	7.58529	-1.275037
H	-7.85524	6.14128	-2.256484
H	-9.08702	6.11393	-0.987246
H	-7.28509	7.6082	1.771654
H	-6.52121	6.17467	2.476327
H	-8.23419	6.13748	2.037019
H	-4.32087	6.22027	0.216152
H	-5.07191	7.65951	-0.492300
H	-4.80398	6.21733	-1.484844
H	5.34581	-6.20648	2.022445
H	4.3708	-6.21415	0.547416
H	5.29962	-7.65247	1.001196
H	5.7794	-6.19425	-2.269644
H	6.72564	-7.62223	-1.821436
H	7.54443	-6.15387	-2.376502
H	9.27778	-6.11318	0.252813
H	8.48596	-6.12608	1.834715

N	-4.248901	-1.417427	0.014891
C	-6.637984	1.415628	0.015241
C	-7.840598	0.733718	0.010431
C	-7.840985	-0.721686	0.007656
C	-6.638880	-1.404453	0.009910
C	-9.068785	1.454394	0.006528
C	-9.068999	-1.442855	0.001784
C	9.095366	1.453185	-0.000385
C	9.094115	-1.455342	-0.001346
C	-10.109394	2.093153	0.001897
C	-10.107735	-2.084714	-0.003657
C	10.123329	2.112248	-0.004805
C	10.121694	-2.115008	-0.004837
Si	-11.684642	3.050634	-0.013506
Si	-11.672103	-3.059018	-0.013227
Si	11.652205	3.142203	-0.013404
Si	11.650877	-3.144516	-0.010608
C	-11.275765	4.881847	0.200780
C	-12.545865	2.757729	-1.668776
C	-12.771764	2.448822	1.408261
C	-11.584690	-4.347842	1.364539
C	-13.117958	-1.879778	0.279176
C	-11.844033	-3.904009	-1.693653
C	11.350248	4.640134	-1.123766
C	12.011977	3.698955	1.755202
C	13.084372	2.107463	-0.678461
C	11.355113	-4.650926	1.089892
C	12.002593	-3.688163	-1.784931
C	13.085622	-2.113858	0.655240
H	-1.907753	2.557233	0.023245
H	-1.909788	-2.549674	0.015101
H	1.936180	-2.551342	0.013507
H	1.938500	2.555606	0.020420
H	6.645944	-2.493267	0.004956
H	6.648211	2.493224	0.008811
H	-6.617517	2.499406	0.017101
H	-6.619059	-2.488238	0.007763
H	-12.189945	5.486162	0.193136
H	-10.761294	5.065600	1.149399
H	-10.629376	5.242390	-0.605740
H	-13.493331	3.306653	-1.715480
H	-12.765700	1.695811	-1.818063
H	-11.923402	3.090677	-2.505298
H	-12.274501	2.584570	2.373874
H	-13.715632	3.005184	1.435332
H	-13.011209	1.386195	1.300646
H	-12.501279	-4.948010	1.392037
H	-10.741762	-5.030288	1.216301
H	-11.463893	-3.874856	2.344256
H	-14.070124	-2.422225	0.282950
H	-13.169129	-1.117573	-0.505056
H	-13.019780	-1.366874	1.241374
H	-11.004414	-4.579123	-1.887150
H	-12.766260	-4.494613	-1.736484
H	-11.877387	-3.170506	-2.505441
H	12.235978	5.284818	-1.154927
H	11.121695	4.334690	-2.149760
H	10.511233	5.241180	-0.758969
H	12.913896	4.320789	1.787753
H	12.171048	2.841910	2.417237
H	11.184097	4.287619	2.162921
H	14.005731	2.699662	-0.715425
H	13.270155	1.237504	-0.040666

H	8.46706	-7.57895	0.824111
H	7.85761	6.13807	-2.258637
H	8.14833	7.58296	-1.278356
H	9.08896	6.11195	-0.988953
H	6.52296	6.17438	2.473990
H	7.28669	7.60768	1.768695
H	8.2359	6.13713	2.034566
H	4.32255	6.21924	0.213234
H	5.07394	7.65835	-0.495104
H	4.80603	6.21618	-1.487659

5a’

atom	x	y	z
C	0.714146	4.903067	0.001829
C	-0.714058	4.903080	0.001934
C	1.417047	3.727258	0.000043
C	0.721789	2.480201	-0.001753
C	-0.721747	2.480214	-0.001664
C	-1.416982	3.727284	0.000241
N	1.418140	1.333206	-0.003474
C	0.723085	0.190222	-0.005296
C	-0.723086	0.190234	-0.005236
N	-1.418120	1.333232	-0.003326
C	1.437920	-1.067597	-0.007154
C	0.705850	-2.243934	-0.009389
C	-0.705895	-2.243922	-0.009355
C	-1.437944	-1.067571	-0.007070
C	-2.859146	-1.091653	-0.005695
C	2.859122	-1.091703	-0.005853
C	-4.079044	-1.152406	-0.003775
C	4.079020	-1.152462	-0.003984
Si	-5.918812	-1.209023	0.003518
C	-6.490671	-2.053043	1.594527
C	-6.500845	-2.193547	-1.500645
C	-6.579558	0.557802	-0.075730
Si	5.918791	-1.209046	0.003539
C	6.501041	-2.193217	-1.500769
C	6.490474	-2.053412	1.594428
C	6.579510	0.557812	-0.075219
H	1.242460	5.851780	0.003169
H	-1.242355	5.851803	0.003362
H	2.501600	3.699937	-0.000134
H	-2.501536	3.699983	0.000218
H	1.235083	-3.190730	-0.010855
H	-1.235145	-3.190708	-0.010807
H	-6.152245	-1.503377	2.478568
H	-7.584649	-2.108451	1.632027
H	-6.101030	-3.073575	1.665875
H	-6.163246	-1.730010	-2.433066
H	-7.595254	-2.245971	-1.529026
H	-6.117043	-3.218543	-1.478719
H	-6.247238	1.063134	-0.988011
H	-6.233267	1.148678	0.778057
H	-7.675442	0.562931	-0.067542
H	6.163634	-1.729433	-2.433136
H	7.595453	-2.245688	-1.528961
H	6.117186	-3.218200	-1.479167
H	6.152137	-1.503817	2.478548
H	7.584442	-2.109027	1.631934
H	6.100646	-3.073883	1.665618
H	6.233285	1.148415	0.778783
H	6.247108	1.063426	-0.987312
H	7.675395	0.562953	-0.067121

H	12.877258	1.745219	-1.690399
H	12.241032	-5.295761	1.110645
H	11.132658	-4.353609	2.119604
H	10.513980	-5.249140	0.725313
H	12.904442	-4.309588	-1.826172
H	12.158468	-2.826246	-2.441373
H	11.172935	-4.273979	-2.193141
H	14.007427	-2.705823	0.683840
H	13.268061	-1.239360	0.022715
H	12.882950	-1.758797	1.670615

6a’

atom	x	y	z
C	-7.39776	0.7131	0.00192
C	-7.39655	-0.71483	0.00596
C	-6.22202	1.41605	-0.00187
C	-4.97242	0.72499	-0.00179
C	-4.97121	-0.72255	0.00219
C	-6.2196	-1.41577	0.00606
N	-3.82904	1.42908	-0.00526
C	-2.68628	0.72543	-0.00478
C	-2.68511	-0.71903	-9.82E-4
N	-3.82661	-1.42467	0.00242
C	-1.44133	1.41554	-0.00763
C	-0.24144	0.73483	-0.00668
C	-0.24032	-0.72429	-0.00325
C	-1.43902	-1.40705	-6.18E-4
C	0.9877	1.45436	-0.00771
C	0.98945	-1.44296	-0.00239
C	2.02916	2.09169	-0.00744
C	2.02995	-2.08192	-0.00163
Si	3.6043	3.04869	0.00159
Si	3.59594	-3.05292	-3.82E-4
C	4.47529	2.75201	1.65117
C	4.68427	2.45091	-1.42741
C	3.1947	4.88066	-0.20572
C	5.03882	-1.87085	-0.29662
C	3.77762	-3.90124	1.67743
C	3.50565	-4.33957	-1.38014
H	-8.34653	1.24124	0.00193
H	-8.34442	-1.24459	0.00898
H	-6.19665	2.50071	-0.00492
H	-6.19236	-2.50038	0.00909
H	-1.46234	2.49933	-0.01012
H	-1.45828	-2.49087	0.00204
H	5.42298	3.30088	1.69384
H	3.85758	3.08275	2.49209
H	4.696	1.68973	1.79657
H	5.62701	3.00893	-1.45926
H	4.18116	2.58691	-2.38995
H	4.92617	1.38856	-1.32247
H	2.67544	5.06691	-1.15124
H	2.55227	5.23896	0.60495
H	4.1089	5.48498	-0.20101
H	5.99191	-2.41164	-0.30463
H	4.93616	-1.35683	-1.25775
H	5.09153	-1.10956	0.4884
H	4.70101	-4.49043	1.71445
H	2.94004	-4.5781	1.87369
H	3.81379	-3.16939	2.4906
H	2.66477	-5.02401	-1.22942
H	3.37945	-3.86505	-2.35843
H	4.42336	-4.93777	-1.41279

7. Fabrication and characterization of thin films and thin film transistors

To fabricate thin-film transistors, the dielectric layer was first formed following the reported method [13] as detailed below.

A solution of $Al(NO_3)_3$ $9H_2O$ in ethanol (0.15 mol/L) was first spin-cast onto a highly doped silicon substrate, which had a 100 nm-thick layer of SiO_2 on its top. The spin-cast film was then baked at 300 ℃ for 30 minutes to form a thin layer of aluminum oxide (Al_2O_3). To modify the Al_2O_3 layer with a self-assembled monolayer (SAM) of 12-cyclohexyldodecylphosphonic acid (CDPA), [14] the Al_2O_3-coated SiO_2/Si wafer was soaked in a 0.3 mM solution of CDPA in isopropanol at room temperature for 12 hours, then rinsed with isopropanol and dried with a flow of nitrogen. The capacitance per unit area (C_i) of CDPA-Al_2O_3/SiO_2 was measured from a metal-insulator-metal structure, where vacuum-deposited gold (0.2 mm × 1 mm) was the top electrode and the highly doped silicon substrate was the bottom electrode, with the frequency ranging from 100 Hz to 100 kHz. As taken at the lowest frequency (100 Hz), the C_i of CDPA-Al_2O_3/SiO_2 is 26 ± 1 nF/cm^2.

Thin films of **3a-b**, **4a-b**, **5a** and **6a** were fabricated by solution-based processes (drop casting or dip coating) onto the CDPA-Al_2O_3/SiO_2 dielectric. Particularly, optimized thin films of **3b** were fabricated by dropping a solution of **3b** in toluene (1mg/mL) onto a tilted substrate (substrate size: 1cm × 1cm, two drops, tilt angle = ~5^o) and the substrate was covered with a glass dish to allow the solvent to evaporate slowly. To dip-coat thin films of **4a** and **6a** onto CDPA-Al_2O_3/SiO_2, the substrate was immersed vertically in a solution and then pulled up at a constant speed with a LongerPump TJ-3A syringe pump. The optimized conditions for dip coating are: **4a** in CH_2Cl_2/acetone (8/1, v/v, 0.5 mg/mL) with a pulling speed of 100 μm/min; **6a** in CH_2Cl_2/acetone (1/1, v/v, 2 mg/mL) with a pulling speed of 200 μm/min.

The soluiton-processed films were then placed in air and at room temperature overnight to allow solvent residues to evaporate. Top contact drain and source gold electrodes (30 nm) were then vacuum-deposited through a shadow mask onto the organic films using an Edwards Auto 306 vacuum coating system with a Turbomolecular pump at a pressure of 4.0 × 10^{-6} torr or lower, with a deposition rate of ca. 2 nm/min to a thickness about 30 nm as measured by a quartz crystal sensor. During vacuum deposition the distance between source and substrate was 18.5 cm. The resulting conduction channels were 50 μm (L) × 1 mm (W), 100 μm (L) × 1 mm (W), 150 μm (L) × 1 mm (W).

X-ray diffraction from thin films were recorded on a SmartLab X-Ray Refractometer. Polarized optical images of the devices were obtained using a Nikon 50IPOL microscope. The AFM images were collected with a Nanoscope IIIa Multimode Microscope (Digital Instruments) using tapping mode and in air under ambient conditions. To measure mobility under vacuum, the current-voltage measurement was carried out on a JANIS ST-500-20-4TX probe station with a Keithley 4200 Semiconductor Characterization System at room temperature with a background pressure of 1.0 × 10^{-5} torr or lower. The mobilities of **3b** and **4a** were measured from at least 30 channels on more than 3 individual substrates, and the mobility of **6a** was measured from at least 10 channels on more than 3 individual substrates. The measured mobility exhibited negligible dependence on the channel length, which varied

13. X. Xu, Y. Yao, B. Shan, X. Gu, D. Liu, J. Liu, J. Xu, N. Zhao, W. Hu, Q. Miao, *Adv. Mater.* **2016**, *28*, 5276–5283.
14. D. Liu, Z. He, Y. Su, Y. Diao, S. C. B. Mannsfeld, Z. Bao, J. Xu, Q. Miao, *Adv. Mater.* **2014**, *26*, 7190–7196.

from 50 μm to 150 μm.

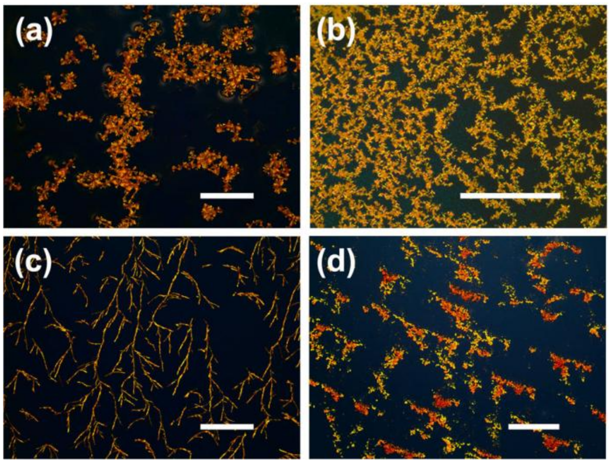


Figure S10. Reflection polarized-light micrographs of thin films of **3a** (a, c) and **4b** (b, d) on CDPA-modified substrates. (a) and (b): fabricated by dropcasting method; (c) and (d): fabricated by dipcoating method. (Scale bar: 200 μm)

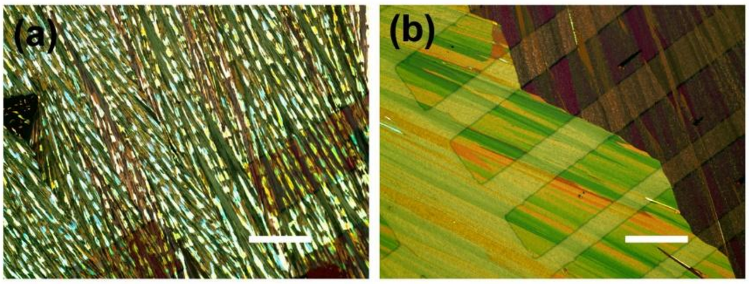


Figure S11. Reflection polarized-light micrographs of crystal thin films of **3b** (a) and **4a** (b) on CDPA-modified substrates. (Scale bar: 200 μm)

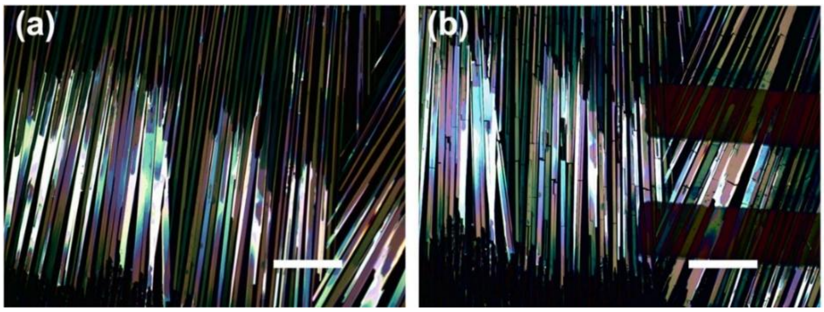


Figure S12. Reflection polarized-light micrographs of crystalline thin films of **6a** on CDPA-modified substrate. (a) Fresh thin film of **6a**; (b) Gold-deposited thin film of **6a**. (scale bar: 200 μm)

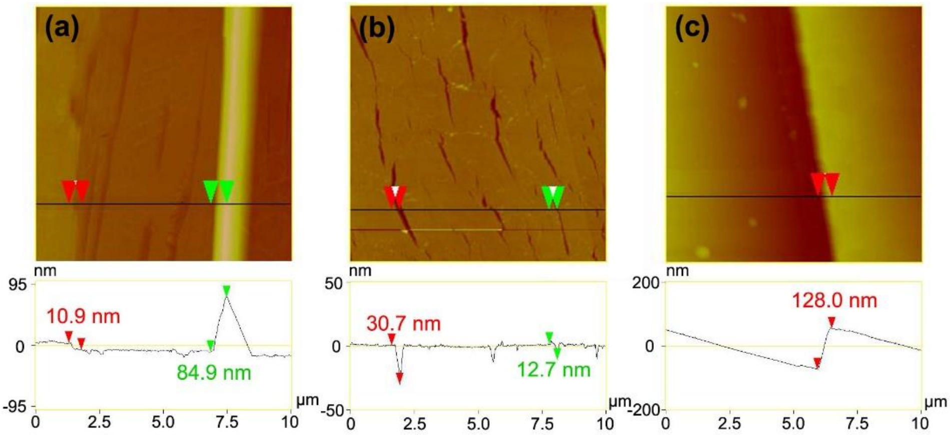


Figure S13. AFM images and section analyses of the thin films of **3b** (a), **4a** (b) and **6a** (c) on CDPA-modified substrates. Each image scale: 10 µm × 10 µm. (Route mean square (RMS) roughness (Rq) is 18.662 nm for **3b**, 3.113 nm for **4a**, and 36.142 nm for **6a**.)

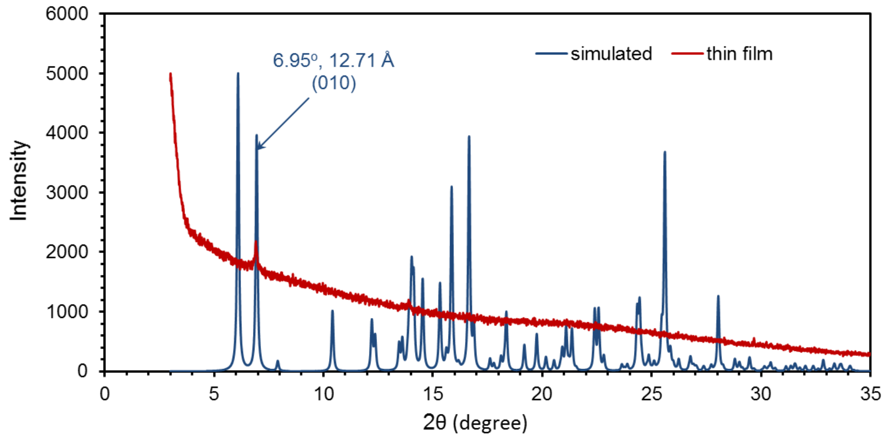


Figure S14 XRD patterns of **3b**. Blue: simulated from single crystal data; Red: dropcasted thin film on the CDPA-modified substrate.

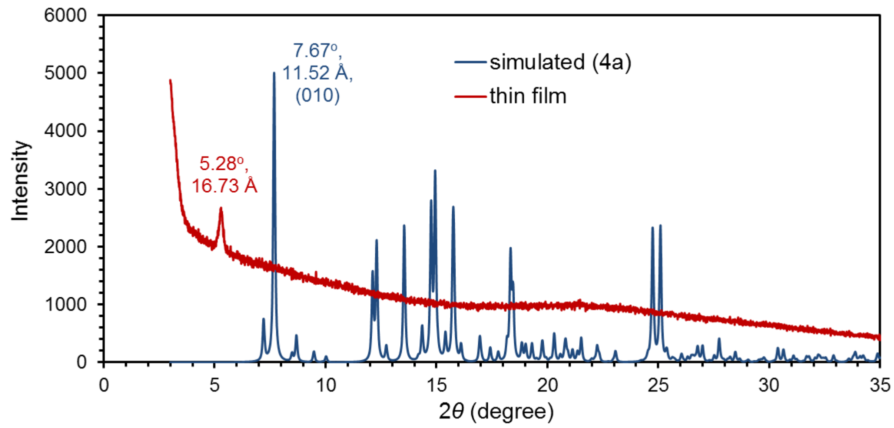


Figure S15. XRD patterns of **4a**. Blue: simulated from single crystal data; Red: dipcoated thin film on the CDPA-modified substrate.

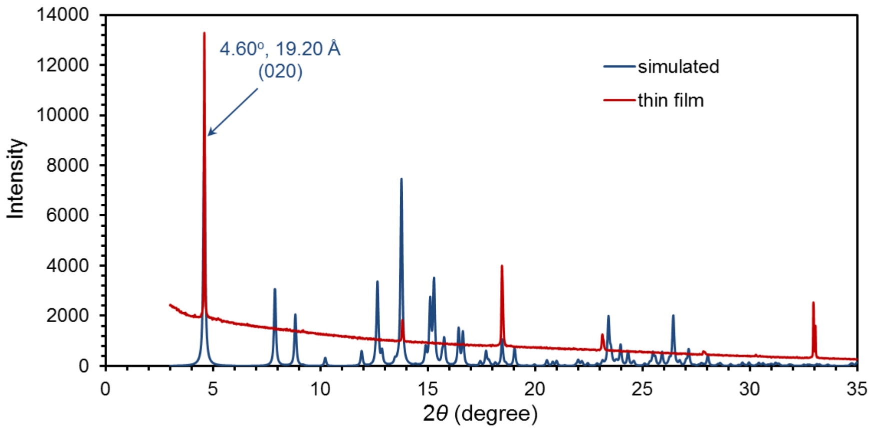


Figure S16. XRD patterns of **6a**. Blue: simulated from single crystal data; Red: dipcoated thin film on the CDPA-modified substrate.

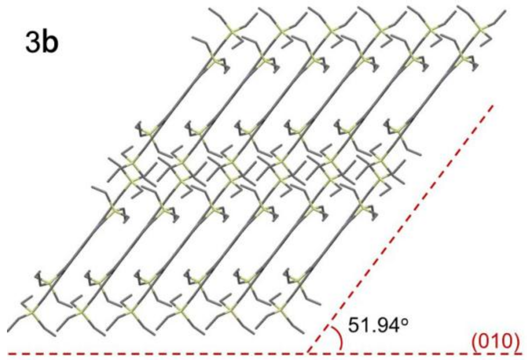


Figure S17. Molecular packing of **3b** with crystal plane (010) labeled. The packing mode propably was adopted in thin films.

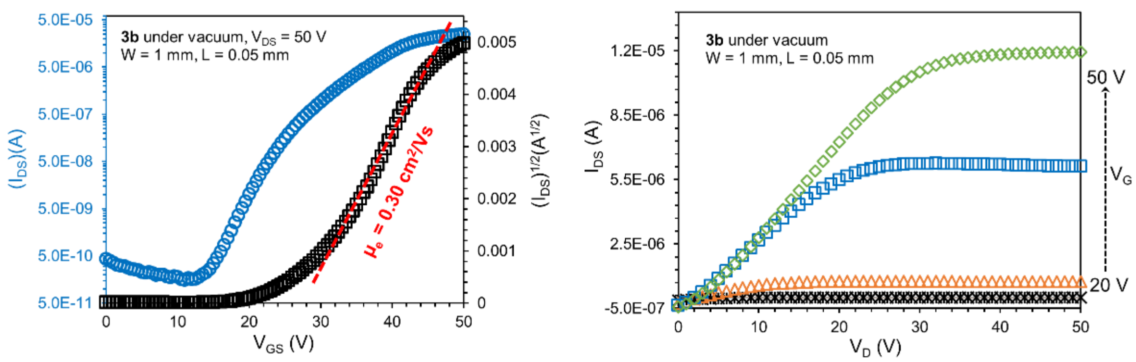


Figure S18. Transfer (a) and Output (b) I-V curves for the best-performing OTFT of **3b** on CDPA-Al_2O_3/SiO_2 as tested under vacuum. During the measurement of transfer I-V curves, a constant drain voltage (V_{DS}) of 50 V was applied.

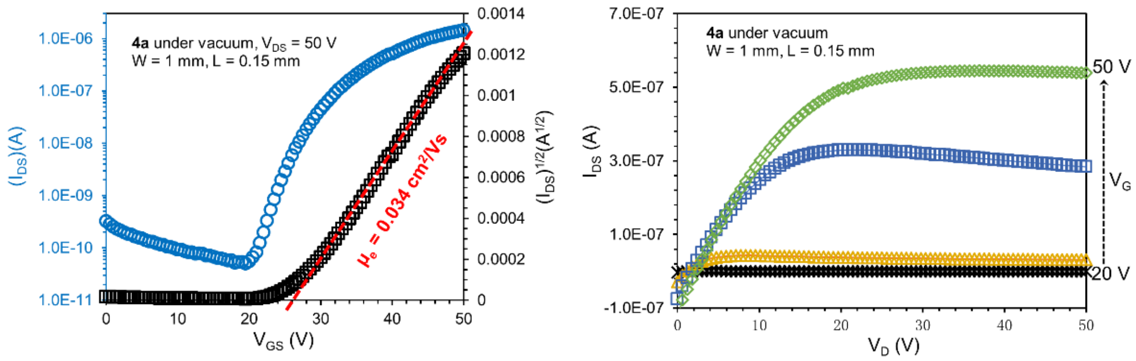
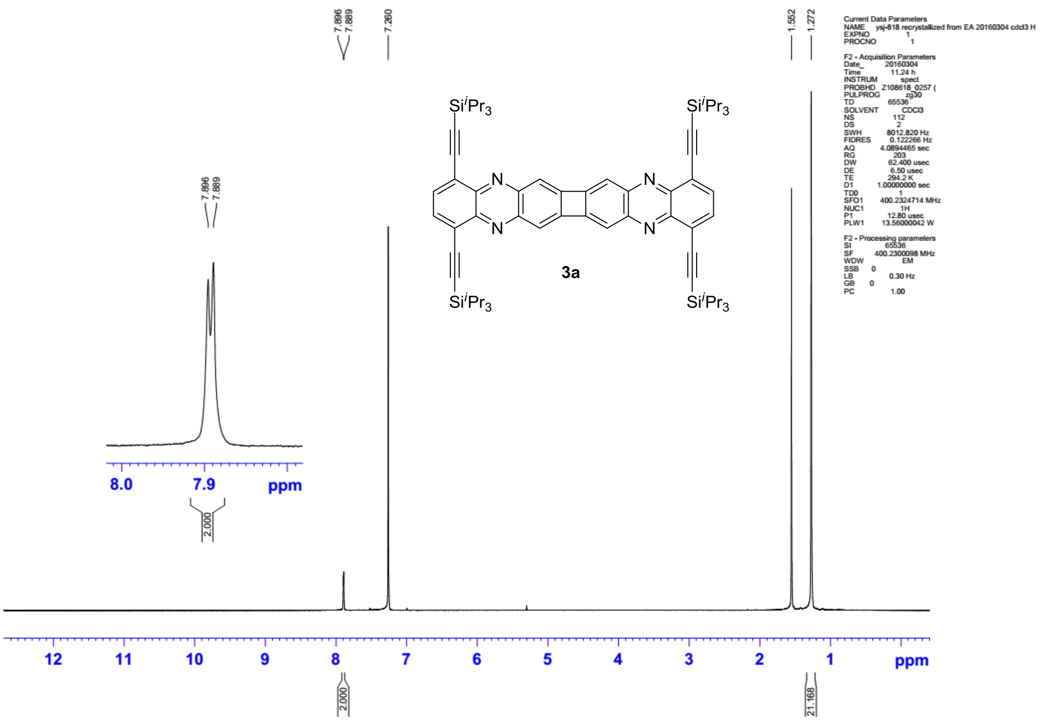
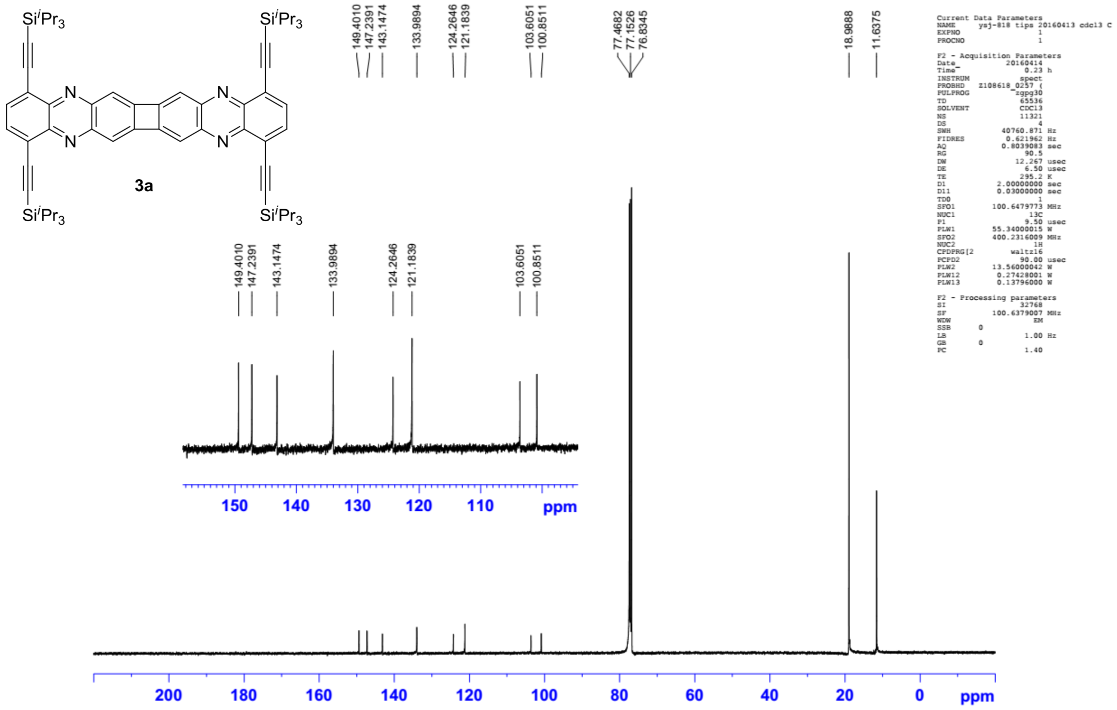


Figure S19. Transfer (a) and Output (b) I-V curves for the best-performing OTFT of **4a** on CDPA-Al_2O_3/SiO_2 as tested under vacuum. During the measurement of transfer I-V curves, a constant drain voltage (V_{DS}) of 50 V was applied.

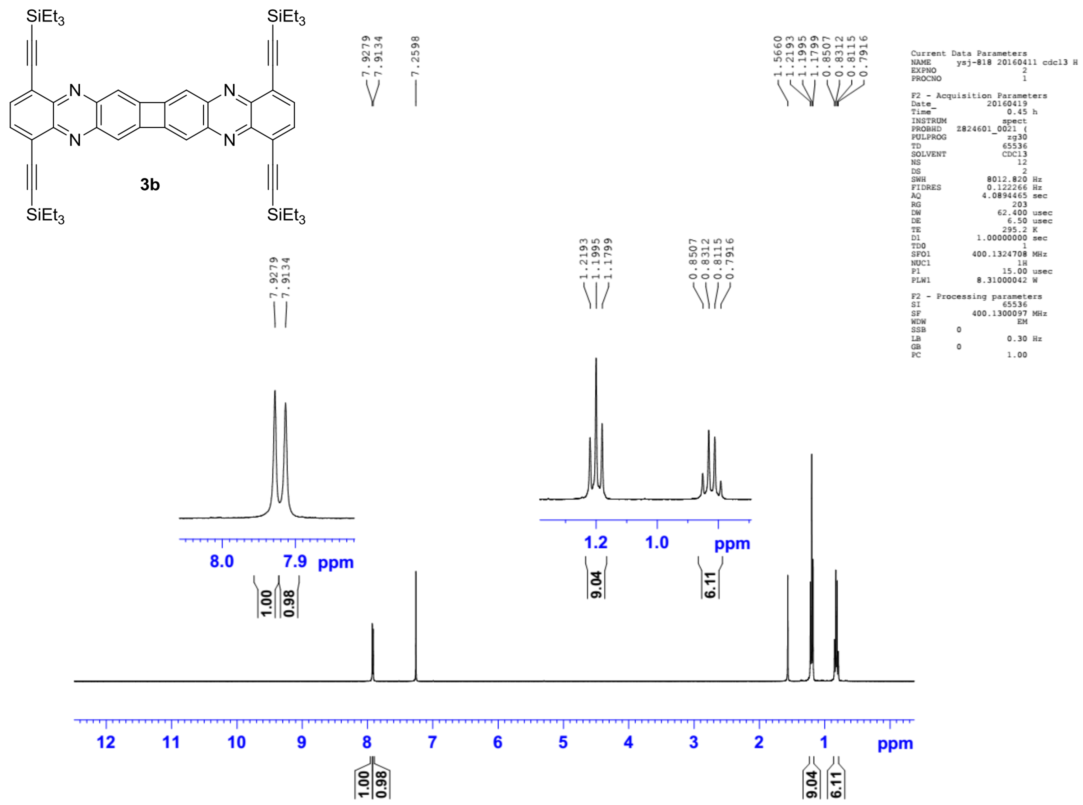
8. NMR spectra



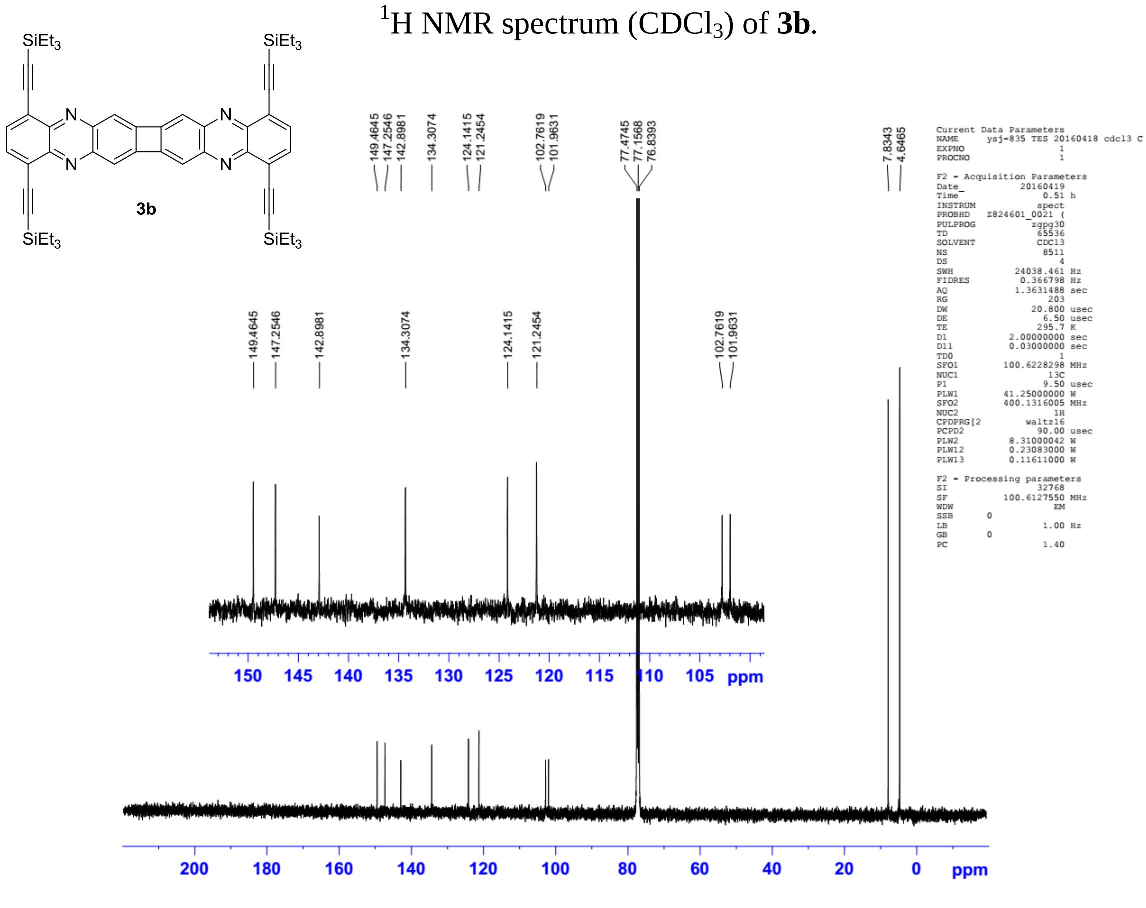
^{1}H NMR spectrum ($CDCl_3$) of **3a**.



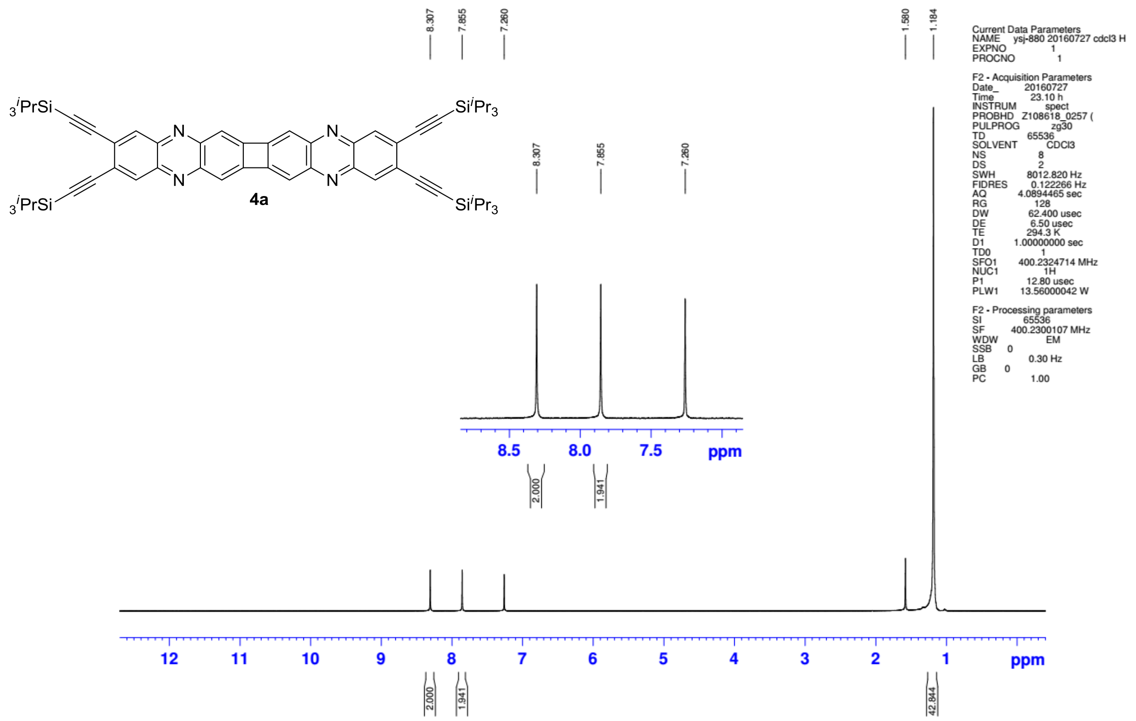
^{13}C NMR spectrum ($CDCl_3$) of **3a**.



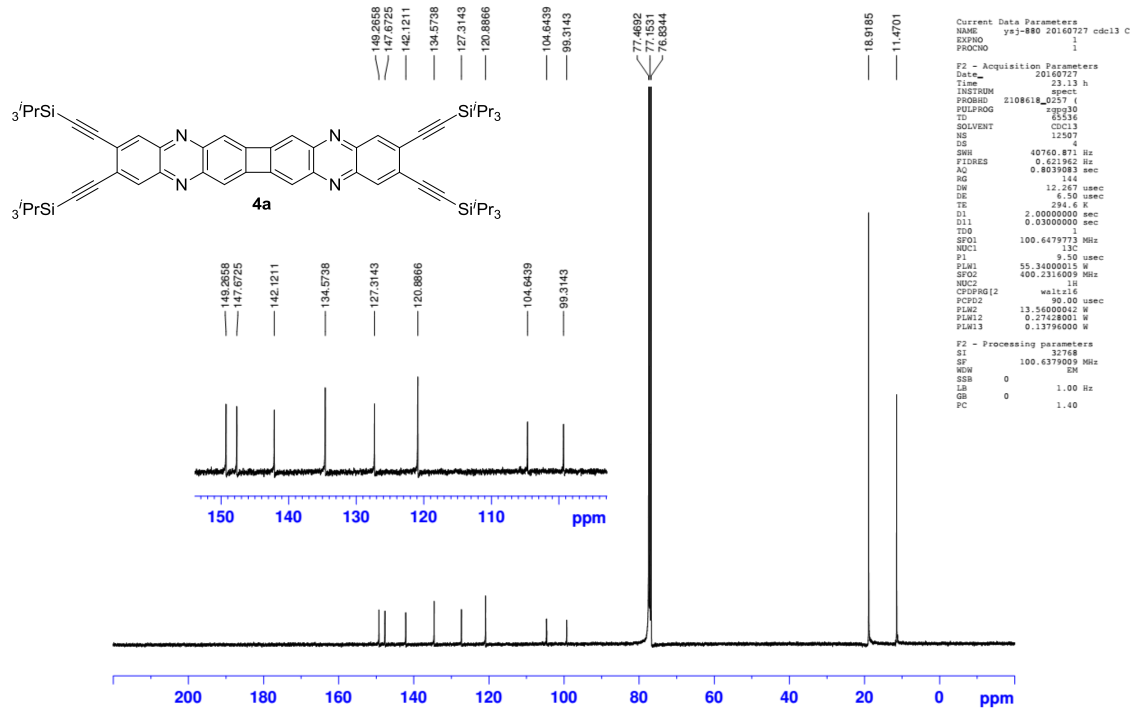
[1]H NMR spectrum ($CDCl_3$) of **3b**.



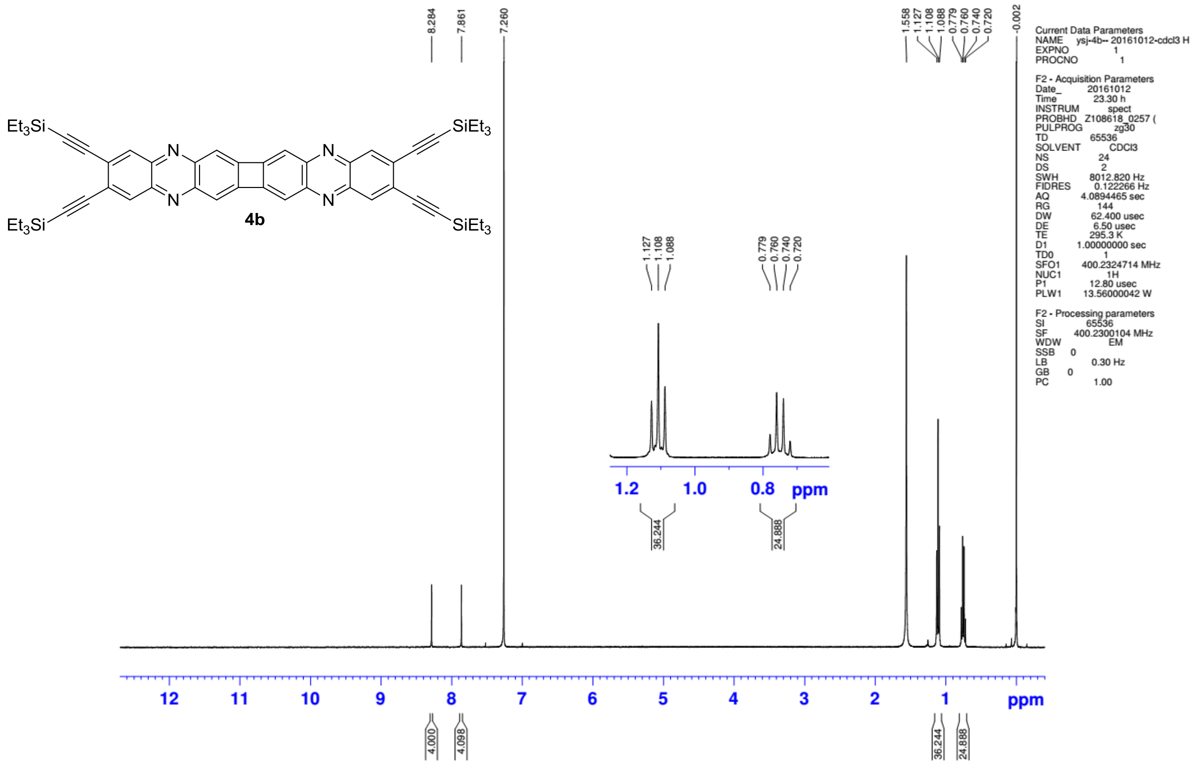
[13]C NMR spectrum ($CDCl_3$) of **3b**.



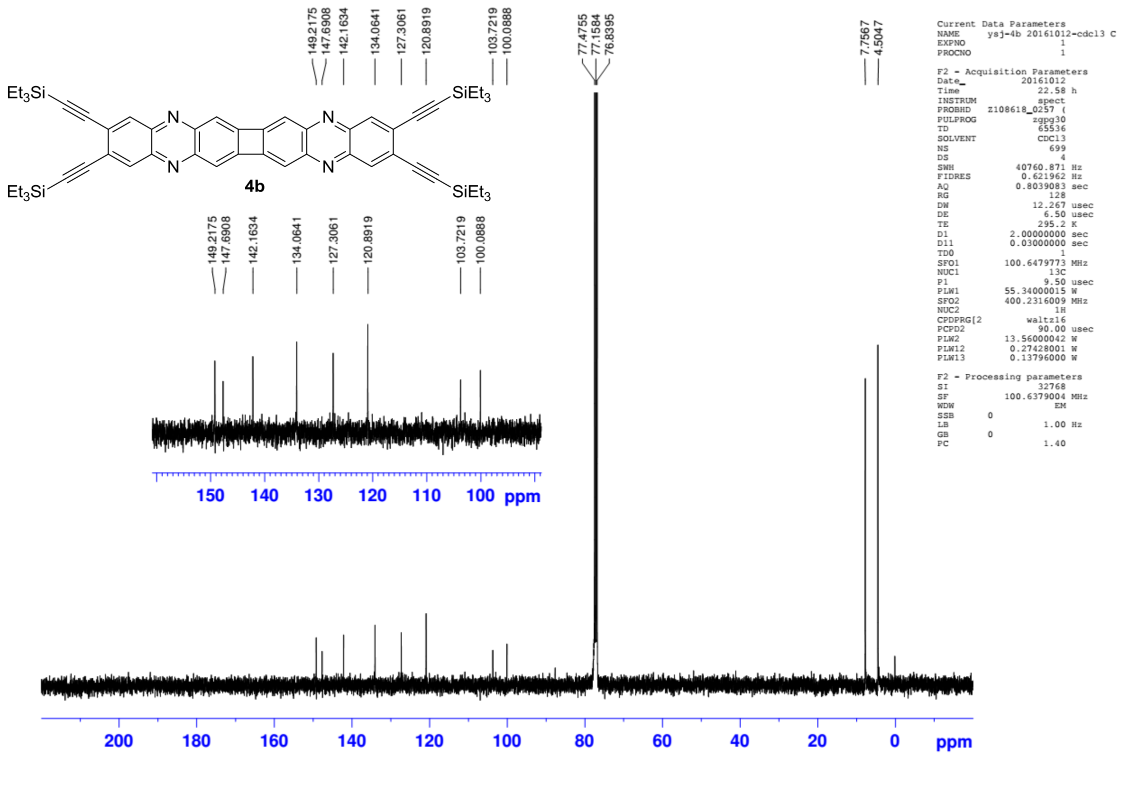
^{1}H NMR spectrum ($CDCl_3$) of **4a**.



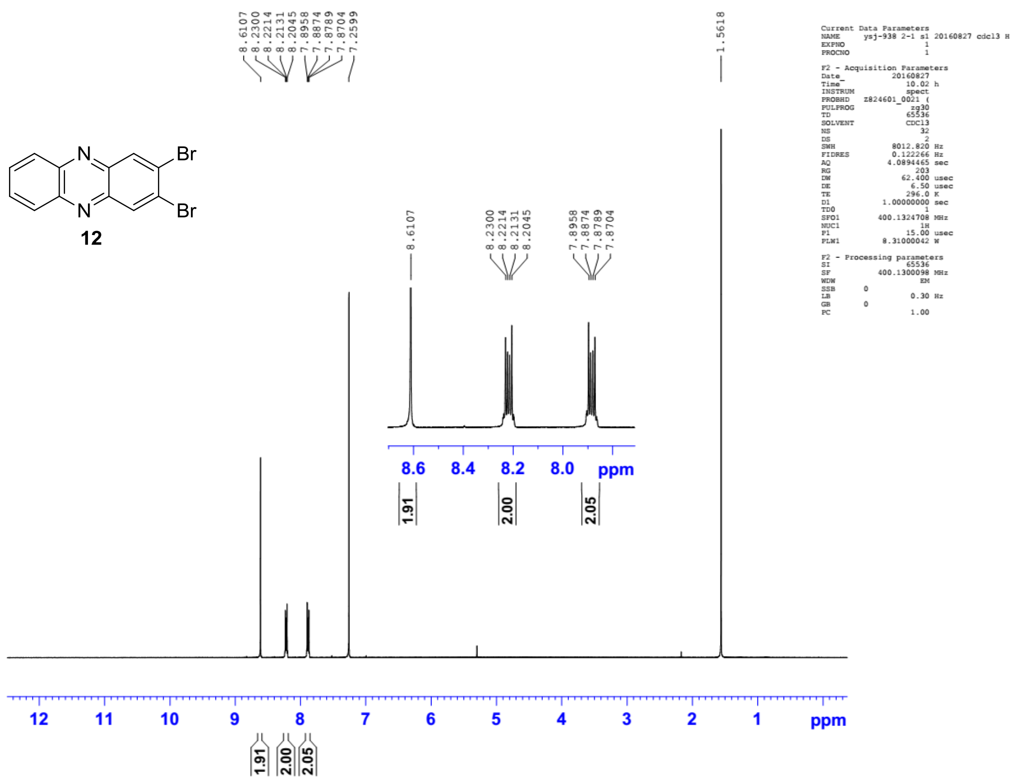
^{13}C NMR spectrum ($CDCl_3$) of **4a**.



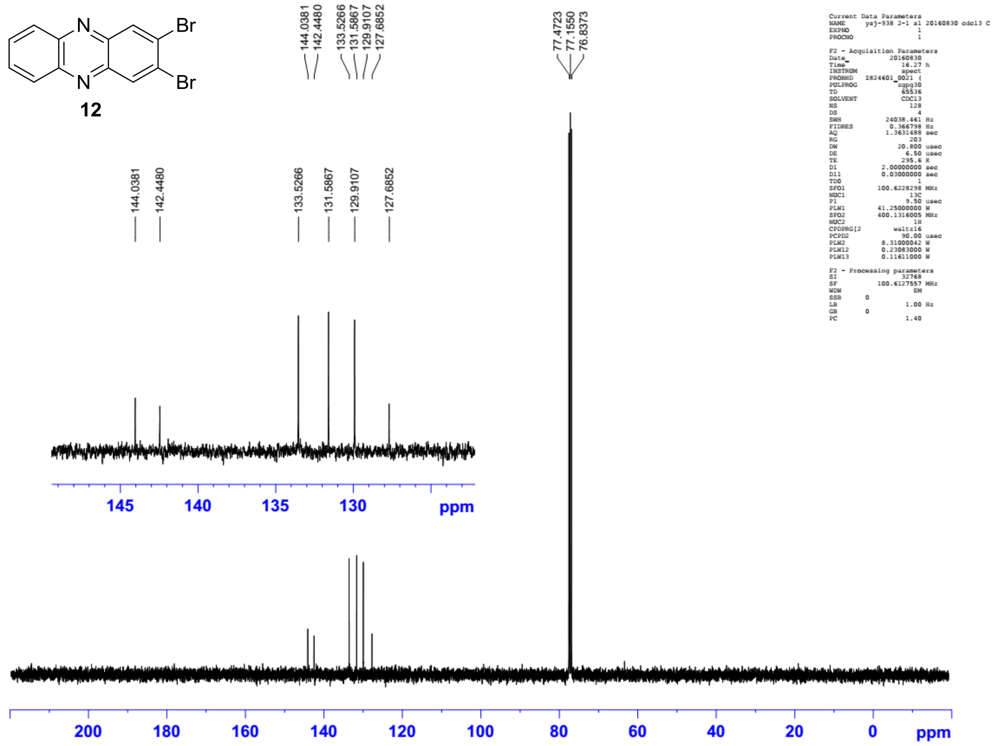
^{1}H NMR spectrum ($CDCl_3$) of **4b**.



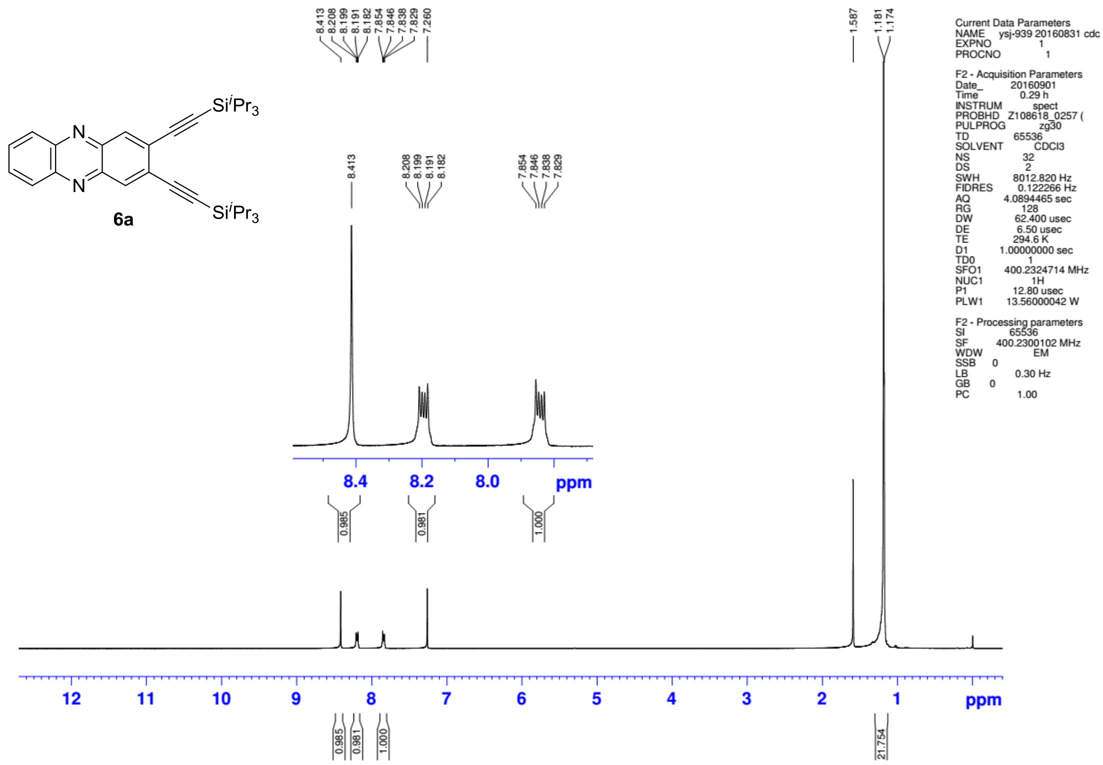
^{13}C NMR spectrum ($CDCl_3$) of **4b**.



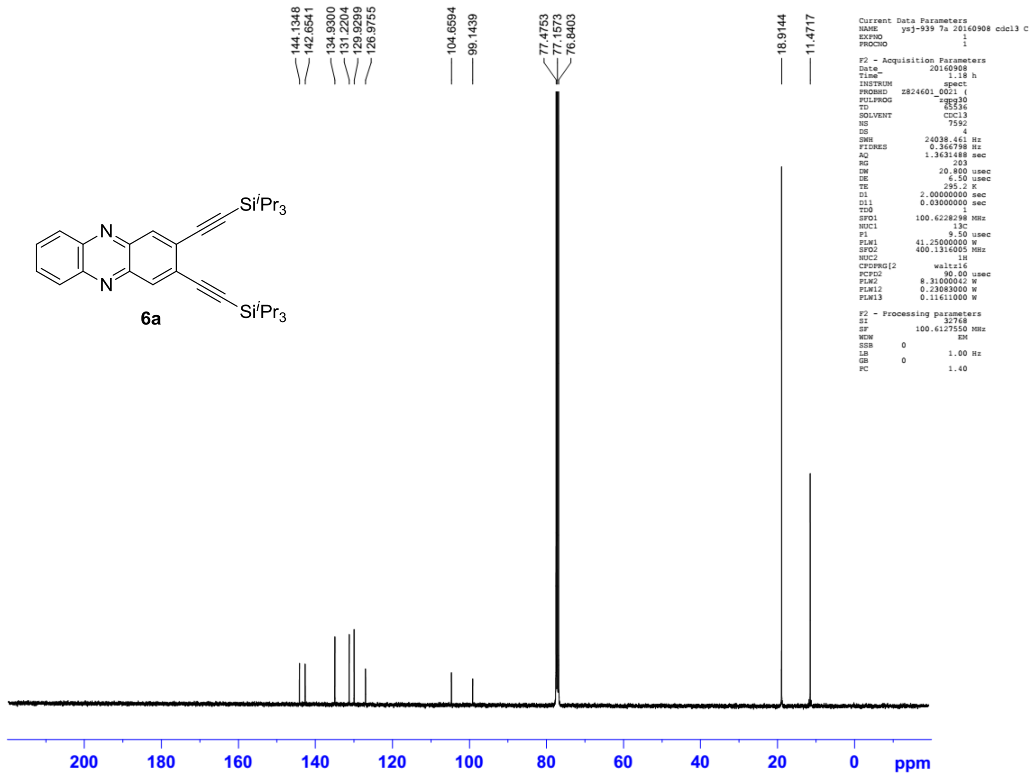
[1]H NMR spectrum ($CDCl_3$) of **12**.



[13]C NMR spectrum ($CDCl_3$) of **12**.



^{1}H NMR spectrum ($CDCl_3$) of **6a**.



^{13}C NMR spectrum ($CDCl_3$) of **6a**.