

Electronic Supplementary Information (ESI):
Substituent effects on the aggregation-induced emission and two-photon absorption properties of triphenylamine-dibenzo[*a,c*]phenazine adducts

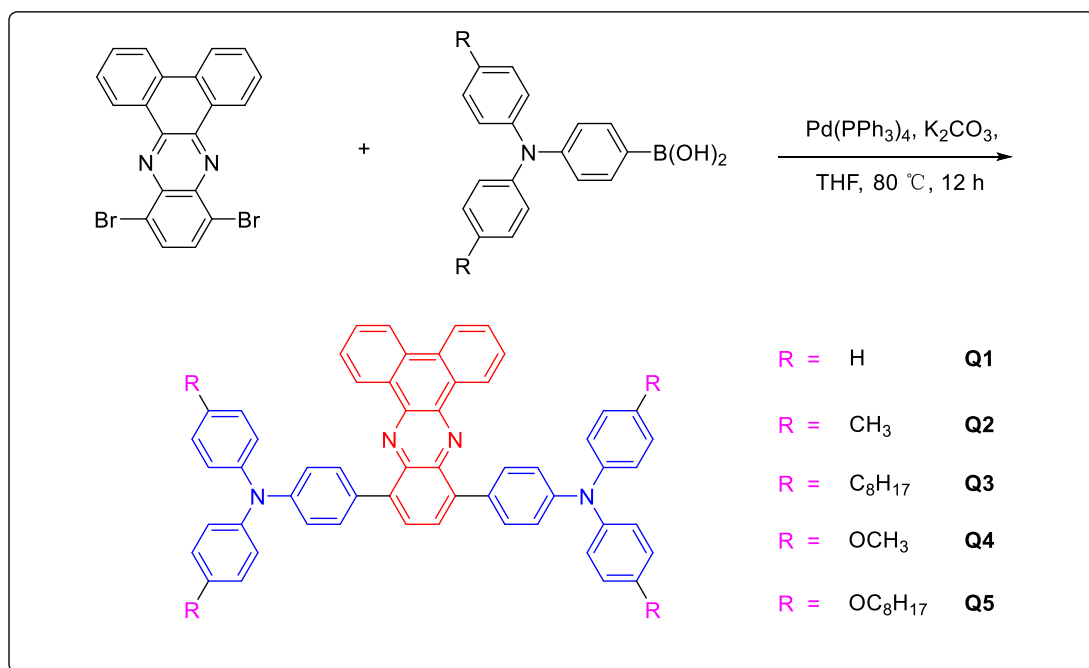
Ji Yang,^a Yuting Gao,^a Tao Jiang,^a Wen Liu,^b Chenchen Liu,^a Niannian Lu,^a Bo Li,^c Ju Mei,^{*a} Qian Peng,^d Jianli Hua^{*a}

^a *Key Laboratory for Advanced Materials, Institute of Fine Chemicals, College of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China. E-mail: daisymeiju@ecust.edu.cn; jlhua@ecust.edu.cn; Fax: +86-21-64250940; Tel: +86-21-64250940*

^b *State Key Laboratory of Modern Optical Instrumentations and Center for Optical and Electromagnetic Research, Zhejiang University, Hangzhou 310058, China*

^c *Key Laboratory of Polar Materials and Devices, Ministry of Education, East China Normal University, Shanghai 200241, China.*

^d *Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*



Scheme S1 Synthetic routes to **Q1–Q5**.

Experimental section

Materials

Synthesis of 4, 4'-(dibenzo[*a,c*]phenazine-10,13-diyl)bis(*N,N*-diphenylaniline)

(Q1). A mixture of 10,13-dibromodibenzo[*a,c*]phenazine (219 mg, 0.5 mmol), (4-(diphenylamino)phenyl)boronic acid (434 mg, 1.0 mmol), and Pd(PPh₃)₄ (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether/DCM (2/1, v/v) as eluent to obtain compound **Q1** (620 mg, 54% yield) as a yellow solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.17 (dd, *J* = 8.0, 1.4 Hz, 4H), 8.00 (s, 2H),

7.94–7.89 (m, 4H), 7.80–7.75 (m, 2H), 7.71–7.66 (m, 2H), 7.34–7.27 (m, 18H), 7.13 (dd, $J = 8.6, 2.5$ Hz, 2H), 7.11–7.06 (m, 4H). HRMS (ESI) (m/z): [M+H] Calcd for $C_{56}H_{39}N_4$: 767.3175, found: 767.3171.

Synthesis of 4, 4'-(dibenzo[*a,c*]phenazine-10,13-diyl)bis(*N,N*-bis(4-octylphenyl)aniline) (Q3). A mixture of 10,13-dibromodibenzo[*a,c*]phenazine (220 mg, 0.5 mmol), (4-(bis(4-octylphenyl)amino)phenyl)boronic acid (520 mg, 1.0 mmol), and $Pd(PPh_3)_4$ (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4 . After removal of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/DCM (1/1, v/v) as eluent to generate **Q3** (350 mg, 57% yield) as an orange solid. 1H NMR (400 MHz, Chloroform-*d*) δ 9.23–9.16 (m, 2H), 8.56 (d, $J = 8.0$ Hz, 2H), 8.00 (s, 2H), 7.90 (d, $J = 8.6$ Hz, 4H), 7.78 (t, $J = 7.5$ Hz, 2H), 7.72–7.66 (m, 2H), 7.34–7.26 (m, 12H), 7.17 (d, $J = 8.6$ Hz, 8H), 1.75 (s, 8H), 1.40 (s, 24H), 0.79 (s, 36H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.72, 144.99, 144.66, 141.03, 140.23, 138.83, 132.15, 131.87, 131.80, 130.73, 130.05, 129.22, 127.95, 127.03, 126.61, 123.95, 122.87, 122.23, 57.25, 38.26, 32.50, 31.82, 31.54. HRMS (ESI) (m/z): [M+H] Calcd for $C_{88}H_{103}N_4$: 1215.8183, found: 1215.8186.

Synthesis of 4, 4'-(dibenzo[*a,c*]phenazine-10,13-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) (Q4). A mixture of 10,13-dibromodibenzo[*a,c*]phenazine (358 mg, 0.8 mmol),

(4-(bis(4-methoxyphenyl)amino)phenyl)boronic acid (570 mg, 1.6 mmol), and Pd(PPh₃)₄ (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether/DCM (1/2, v/v) as eluent to obtain **Q4** (520 mg, 72% yield) as a red solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.18 (dd, *J* = 7.9, 1.5 Hz, 2H), 8.55 (d, *J* = 8.1 Hz, 2H), 7.97 (s, 2H), 7.88 (d, *J* = 8.5 Hz, 4H), 7.81–7.74 (m, 2H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.29–7.26 (m, 4H), 7.16 (q, *J* = 8.7 Hz, 16H), 2.36 (s, 12H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.94, 148.25, 141.03, 140.27, 138.72, 131.79, 130.04, 129.17, 127.96, 126.82, 122.86, 119.83, 114.75, 55.55. HRMS (ESI) (*m/z*): [M+H] Calcd for C₆₀H₄₇N₄O₄: 887.3597, found: 887.3594.

Synthesis of 4, 4'-(dibenzo[*a,c*]phenazine-10,13-diyl)bis(*N,N*-bis(4-(octyloxy)phenyl)aniline) (Q5). A mixture of 10,13-dibromodibenzo[*a,c*]phenazine (173 mg, 0.4 mmol), (4-(bis(4-(octyloxy)phenyl)amino)phenyl)boronic acid (430 mg, 0.8 mmol), and Pd(PPh₃)₄ (21 mg, 0.02 mmol) was dissolved in 15 mL THF under argon atmosphere. Aqueous solution of potassium carbonate (2 M, 5 mL) was added to the reaction solution and stirred at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was extracted by dichloromethane and water (3 × 15 mL). The combined organic layers were washed with water and dried over Na₂SO₄. After removal

of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/DCM (1/2, v/v) as eluent to obtain **Q5** (365 mg, 72% yield) as a red solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.18 (d, $J = 7.9$ Hz, 2H), 8.55 (d, $J = 8.1$ Hz, 2H), 7.95 (s, 2H), 7.85 (d, $J = 8.5$ Hz, 4H), 7.80–7.72 (m, 2H), 7.72–7.65 (m, 2H), 7.24–7.15 (m, 12H), 6.89 (d, $J = 8.8$ Hz, 8H), 3.96 (t, $J = 6.5$ Hz, 8H), 1.86–1.73 (m, 8H), 1.46 (dt, $J = 11.4, 5.3$ Hz, 8H), 1.35–1.27 (m, 32H), 0.89 (t, $J = 6.4$ Hz, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.54, 148.29, 140.9, 140.83, 140.25, 138.69, 132.11, 131.76, 130.76, 130.56, 129.97, 129.13, 127.94, 126.82, 126.62, 124.48, 124.00, 122.82, 119.70, 115.30, 68.31, 31.86, 30.22, 29.43, 29.29, 26.14, 22.70, 14.14. HRMS (ESI) (m/z): [M+H] Calcd for $\text{C}_{88}\text{H}_{103}\text{N}_4\text{O}_4$: 1279.7979, found: 1279.7971.

Characterization:

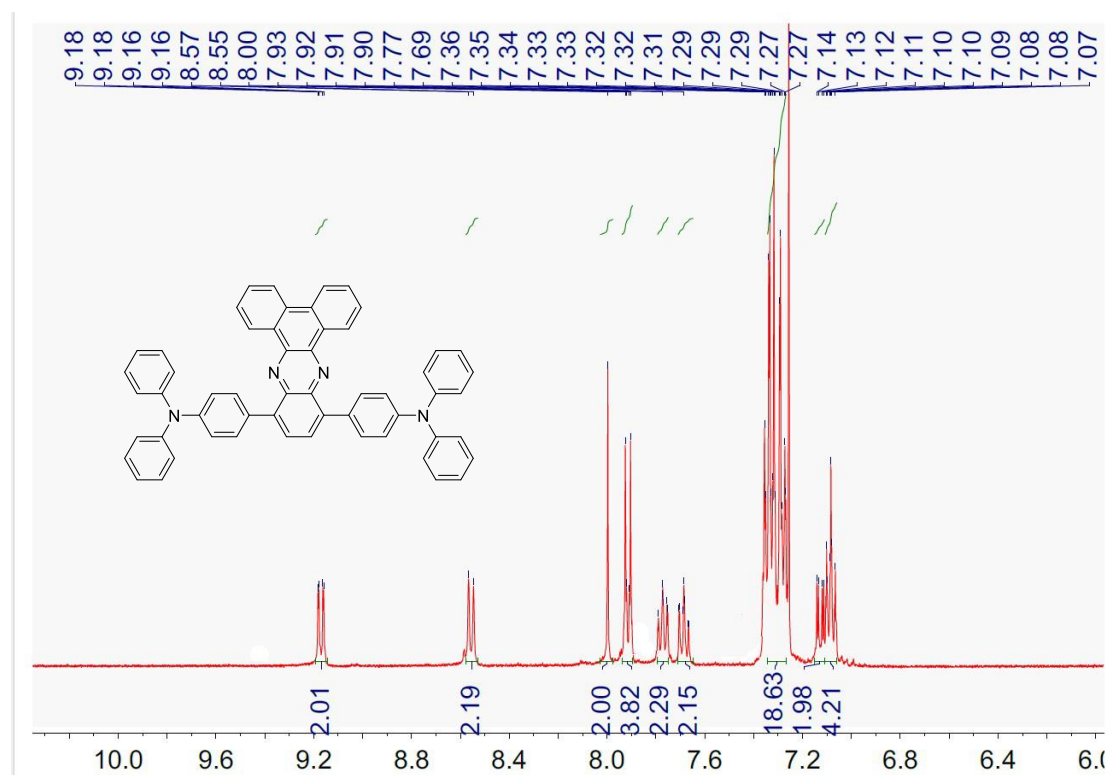


Fig. S1 ^1H NMR of **Q1**.

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-56 H: 0-80 N: 0-4
HUA-JL

ECUST institute of Fine Chem

21-Nov-2014
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1.90e+003

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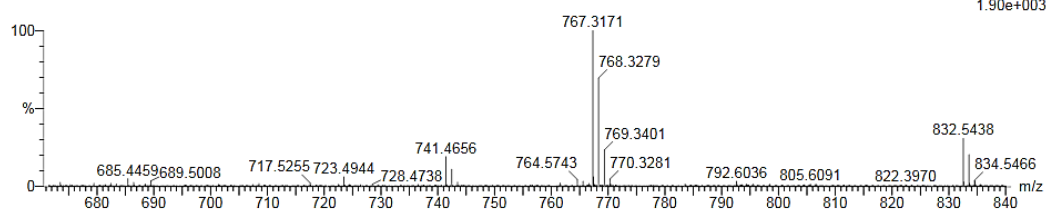


Fig. S2 High-res ESI-TOF mass spectrum of **Q1**.

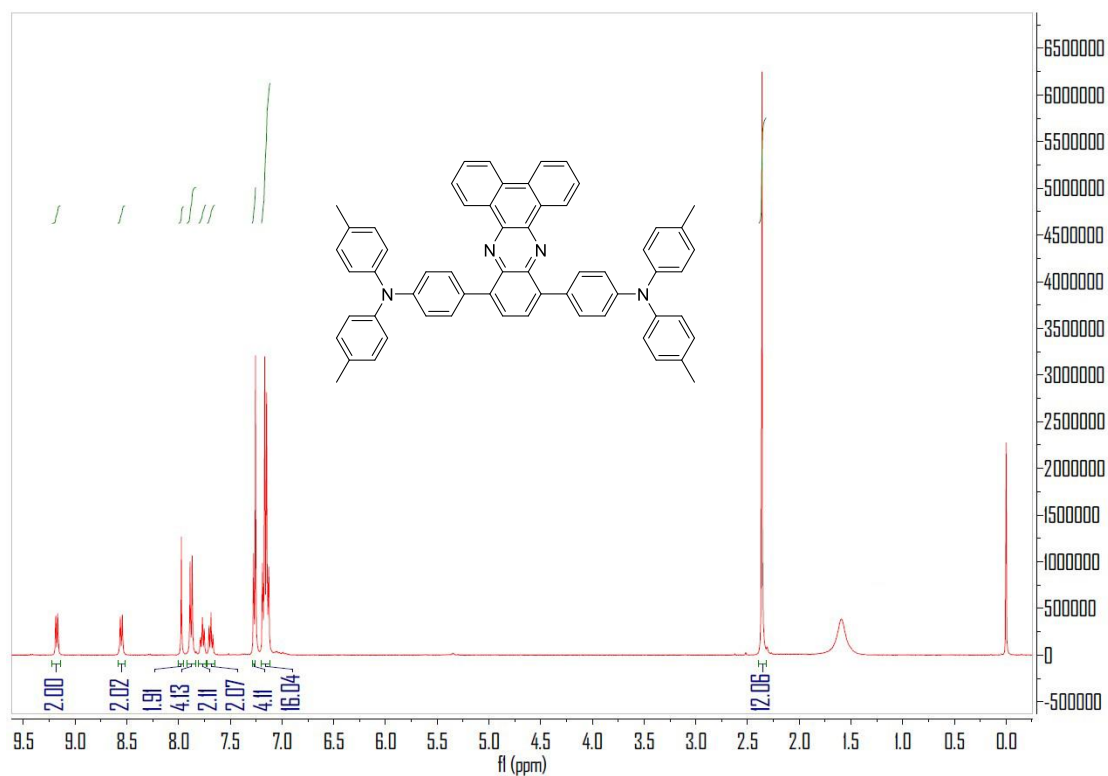


Fig. S3 ^1H NMR of **Q2**.

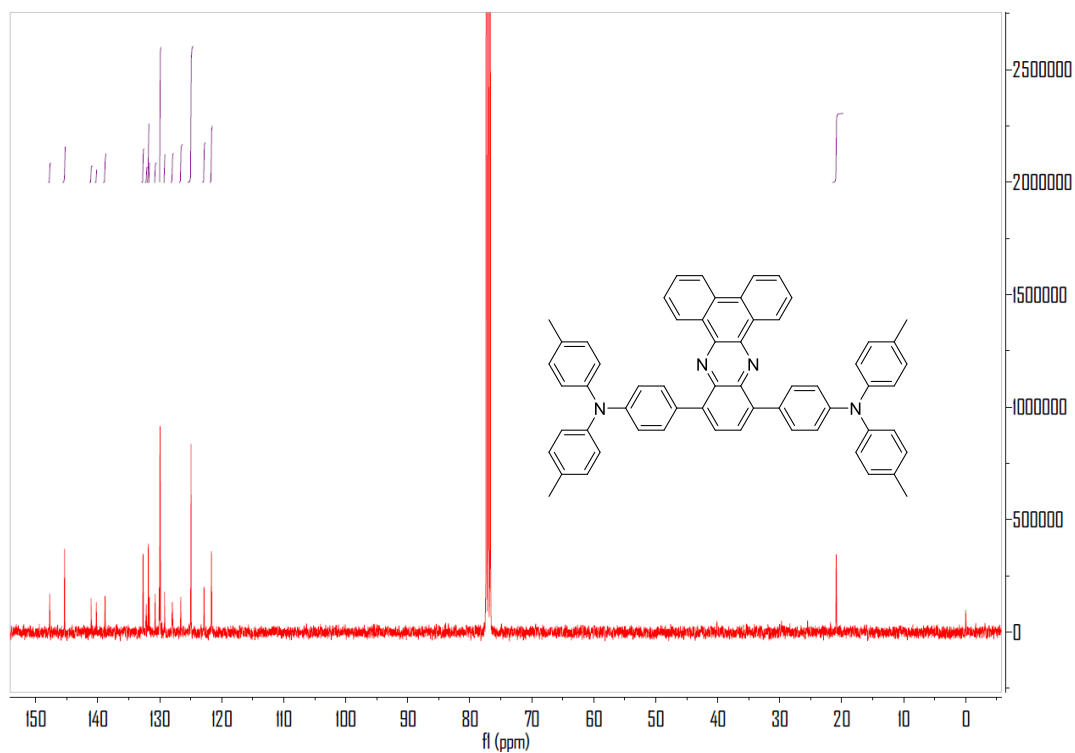


Fig. S4 ^{13}C NMR of compound Q2.

Monoisotopic Mass, Even Electron Ions

6 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-60 H: 0-80 N: 0-4

JL-HUA

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08-Jul-2016

10:05:03

1: TOF MS ES+

1.56e+004

HL-YJ-M441 29 (0.274) Cm (15:41)

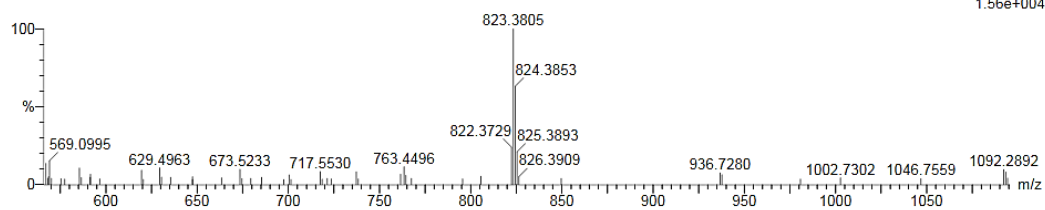


Fig. S5 High-res ESI-TOF mass spectrum of Q2.

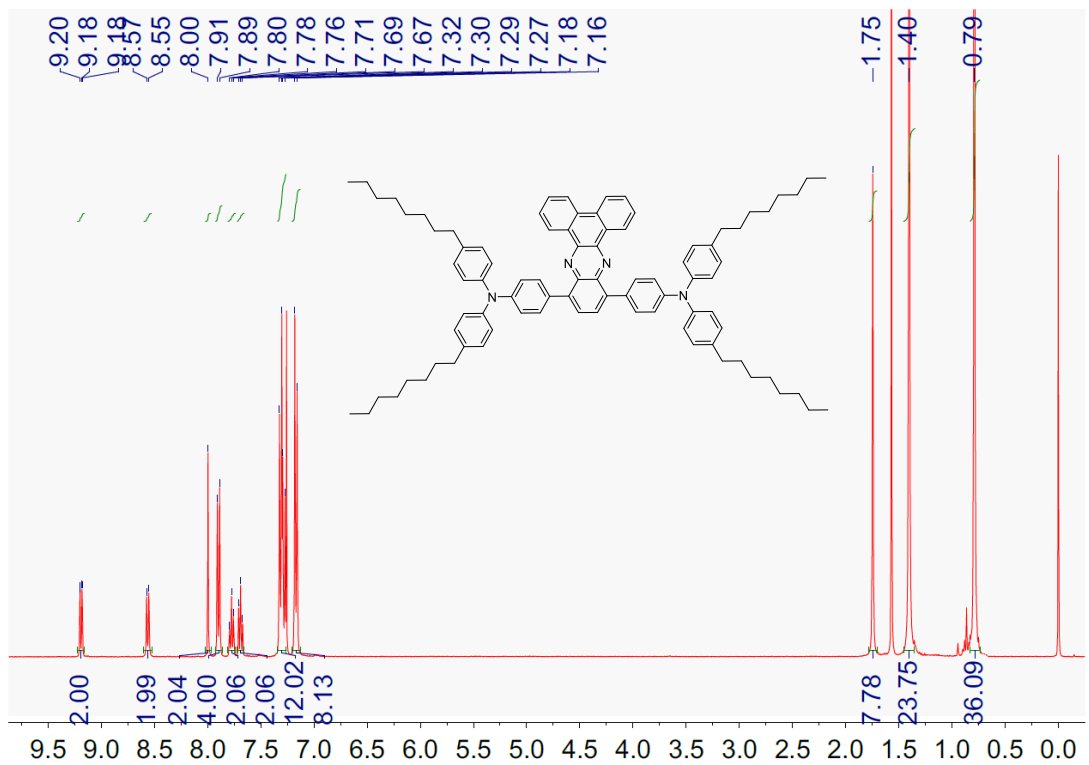


Fig. S6 ^1H NMR of Q3.

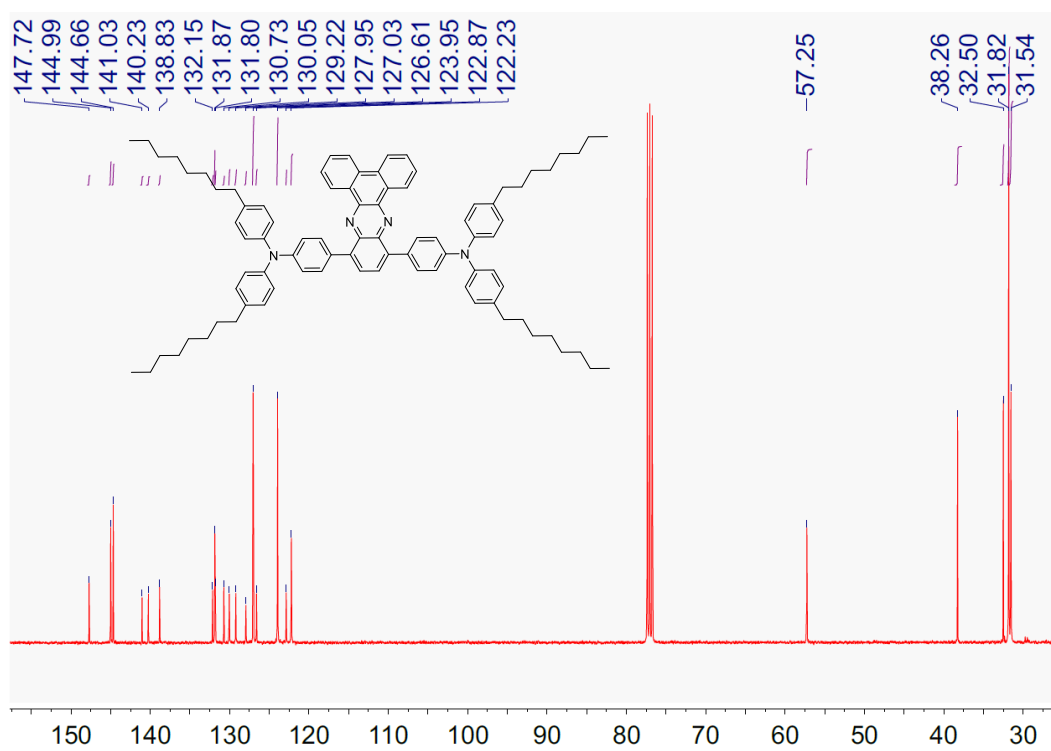


Fig. S7 ^{13}C NMR of compound Q3.

Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)
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HUA-JL
ECUST institute of Fine Chem
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21-Nov-2014
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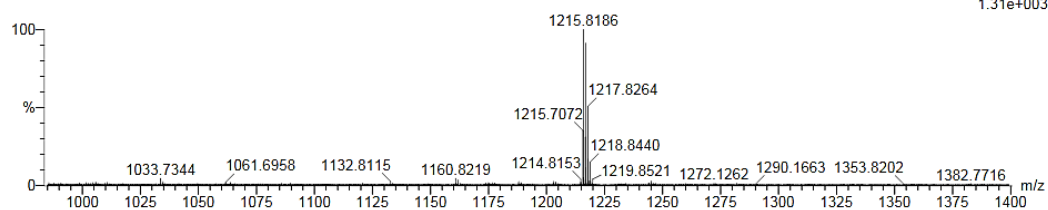


Fig. S8 High-res ESI-TOF mass spectrum of **Q3**.

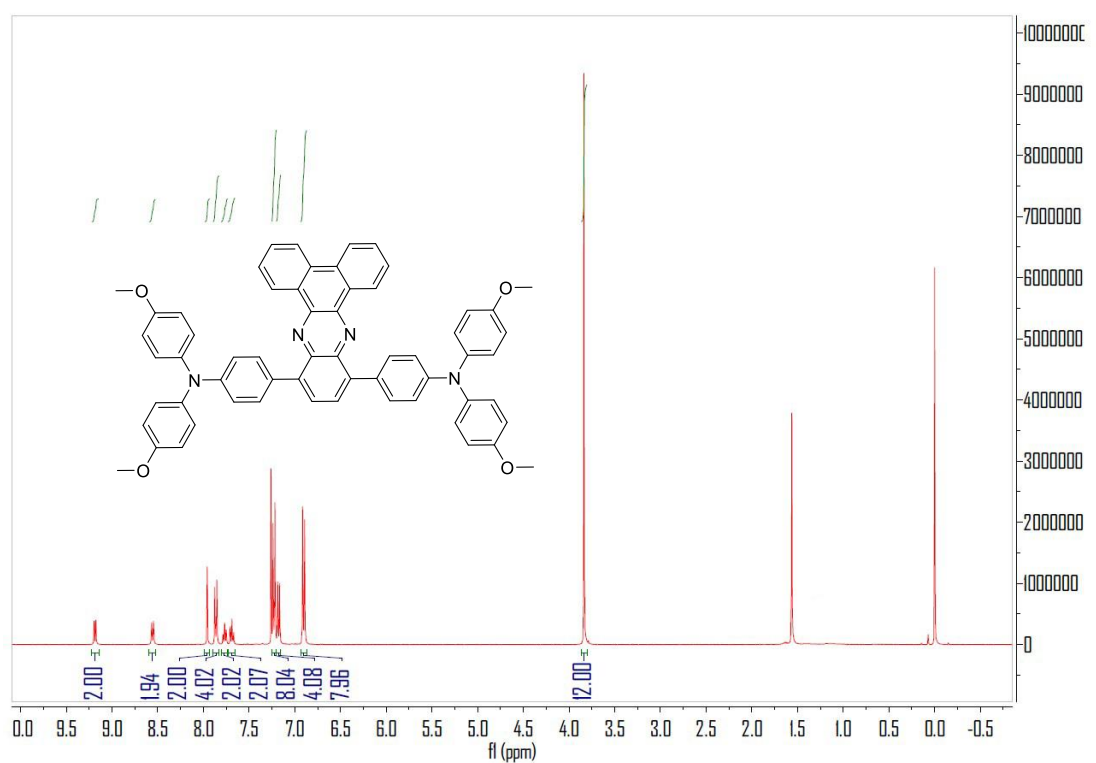


Fig. S9 ^1H NMR of **Q4**.

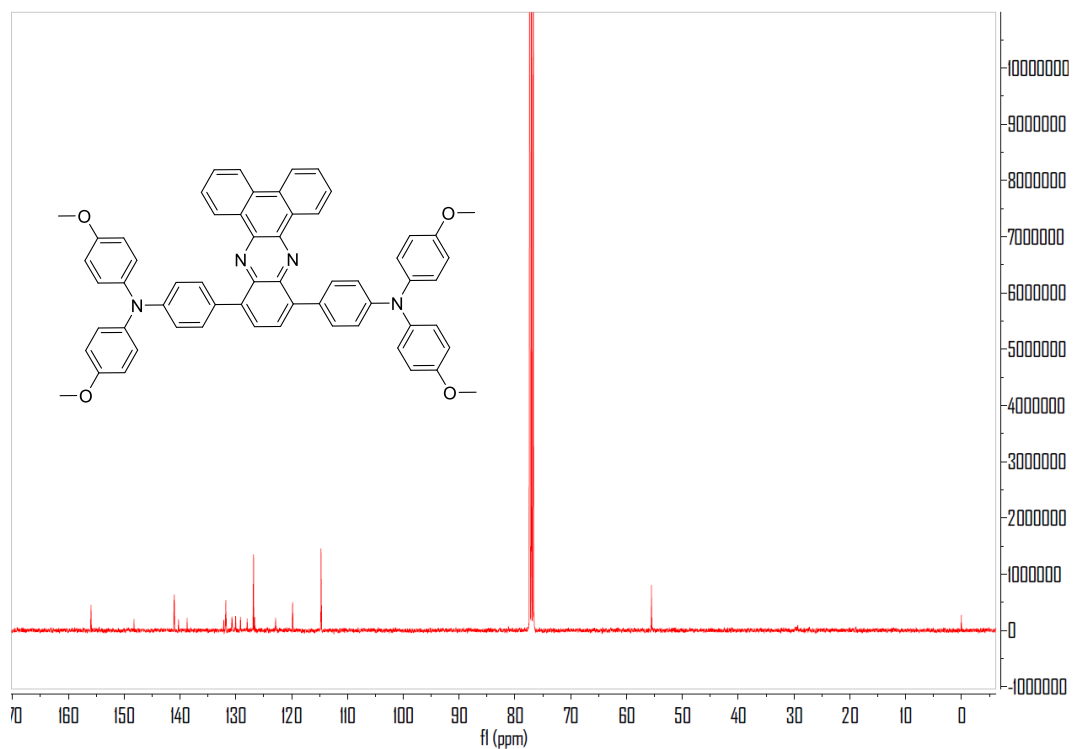


Fig. S10 ^{13}C NMR of compound **Q4**.

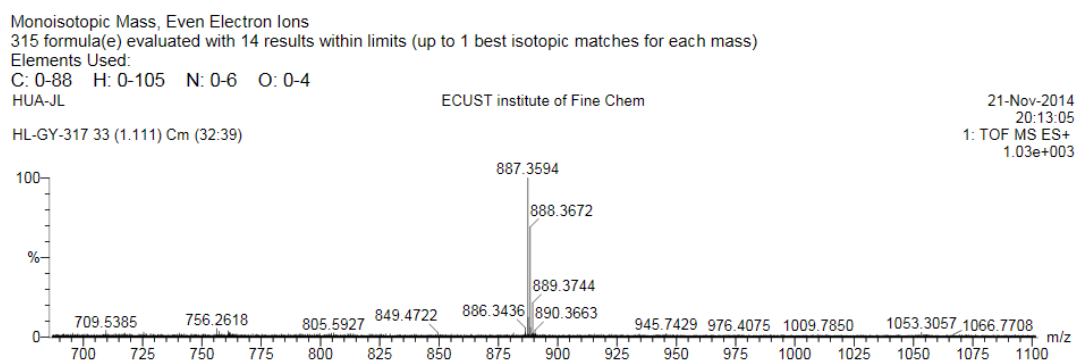


Fig. S11 High-res ESI-TOF mass spectrum of **Q4**.

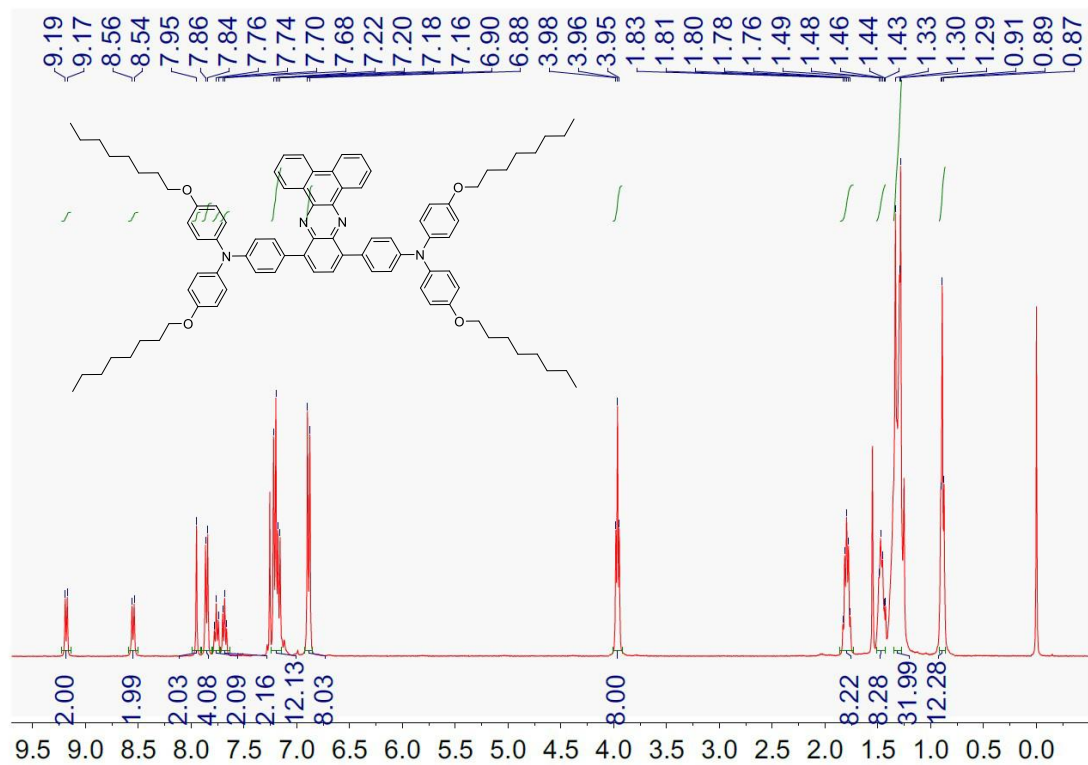


Fig. S12 ¹H NMR of Q5.

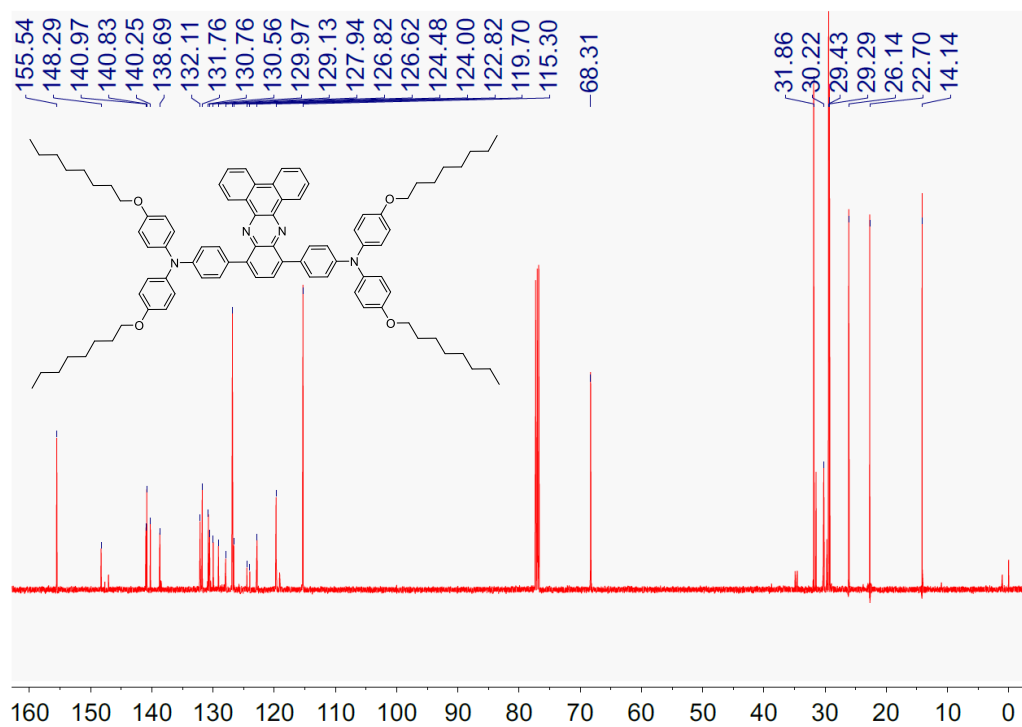


Fig. S13 ¹³C NMR of compound Q5.

Monoisotopic Mass, Even Electron Ions
15 formula(e) evaluated with 3 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-88 H: 0-105 N: 0-6 O: 0-4
HUA-JL

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21-Nov-2014
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2.96e+003

HL-GY-310 28 (0.937) Cm (28:32)

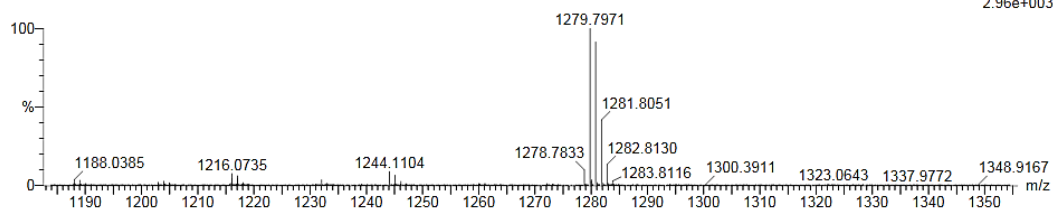


Fig. S14 High-res ESI-TOF mass spectrum of **Q5**.