Electronic Supplementary Information for

Dicyanopyrazine Capped with Tetraphenylethylene: Polymorphs with High Contrast Luminescence as Organic Volatile Sensor

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Table of Contents

7. **Fig. S7** The XRD patterns of **2DQCN** crystalline films before and after exposure to CH_2Cl_2 and cyclohexane solvents.
8. **Synthesis**
9. **NMR Spectra of Compound (4), (5), 1DQCN, 2DQCN. (Fig. S8-Fig. S15)**
10. **High Resolution Mass Spectra of 1DQCN and 2DQCN. (Fig. S16-Fig. S17)**
11. **Reference**

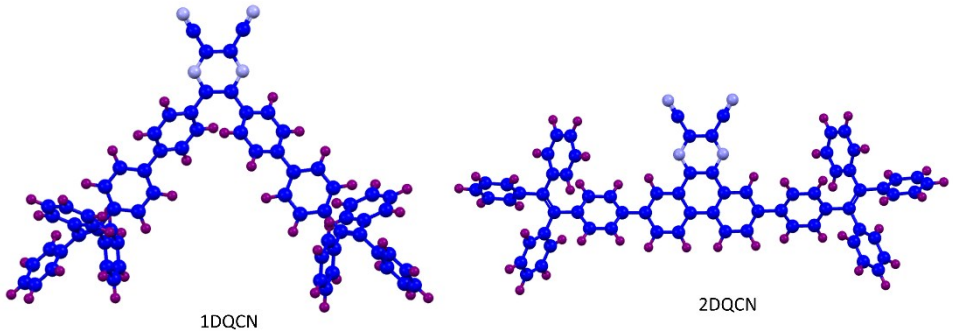


Fig. S1 The geometry-optimized molecular structure plots (optimized by using density functional theory calculation at the DFT/B3LYP/6-31G(d) level).

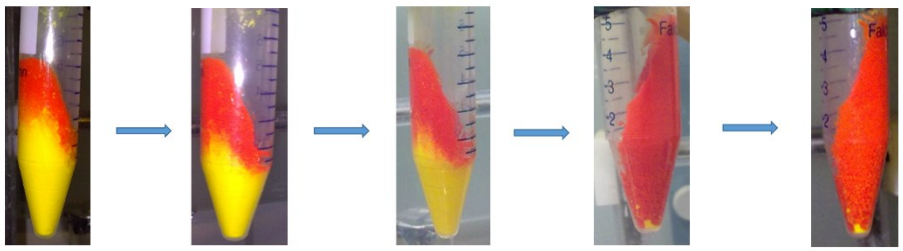


Fig. S2 The whole transformation process of **2DQCN** from yellow to red in the

centrifuge tube.

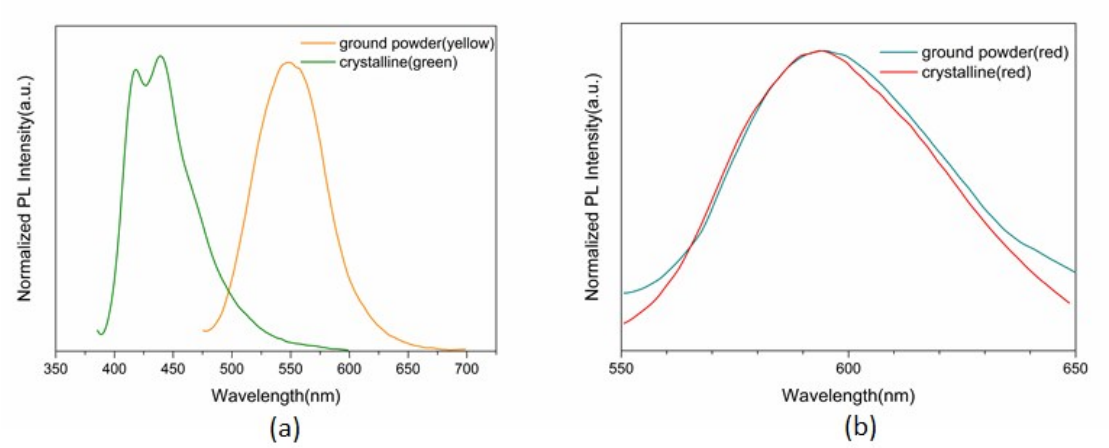


Fig. S3 Fluorescence spectra of (a) **1DQCN** and (b) **2DQCN** before and after grinding.

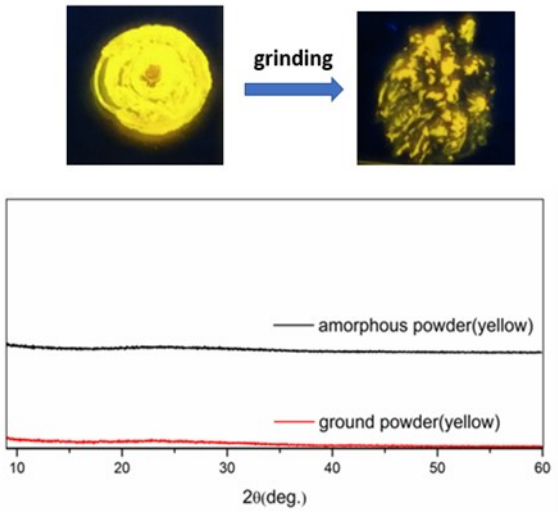


Fig. S4 The fluorescence images and PXRD patterns of **2DQCN** amorphous state before and after grinding.

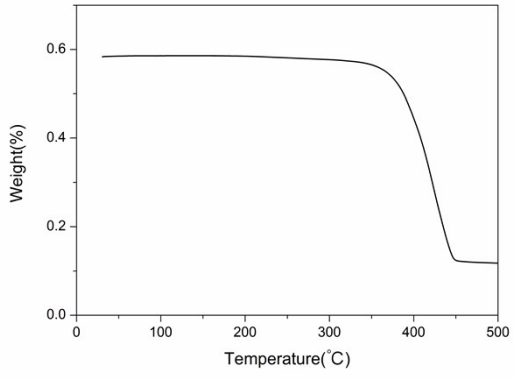


Fig. S5 TGA thermogram of **2DQCN** recorded under N_2 atmosphere at a heating rate of 10 ℃/min.

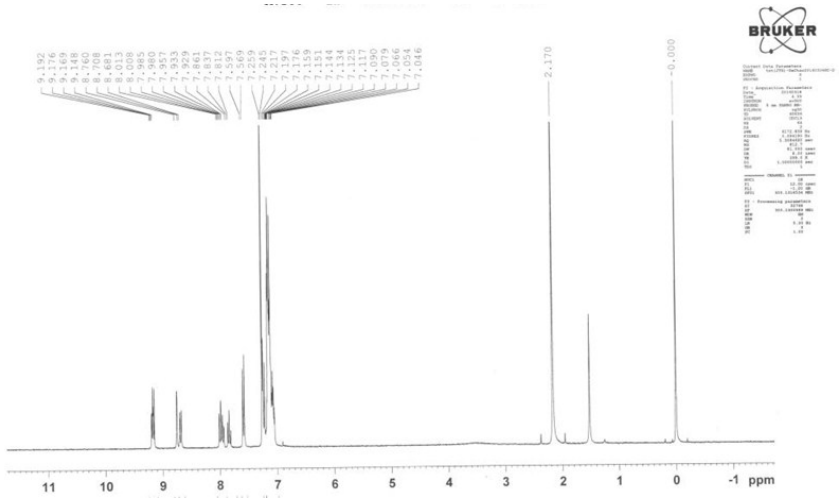


Fig. S6 ^{1}H NMR spectra of **2DQCN** in chloroform-*d* after annealing at 260 ℃ for more than ten minutes.

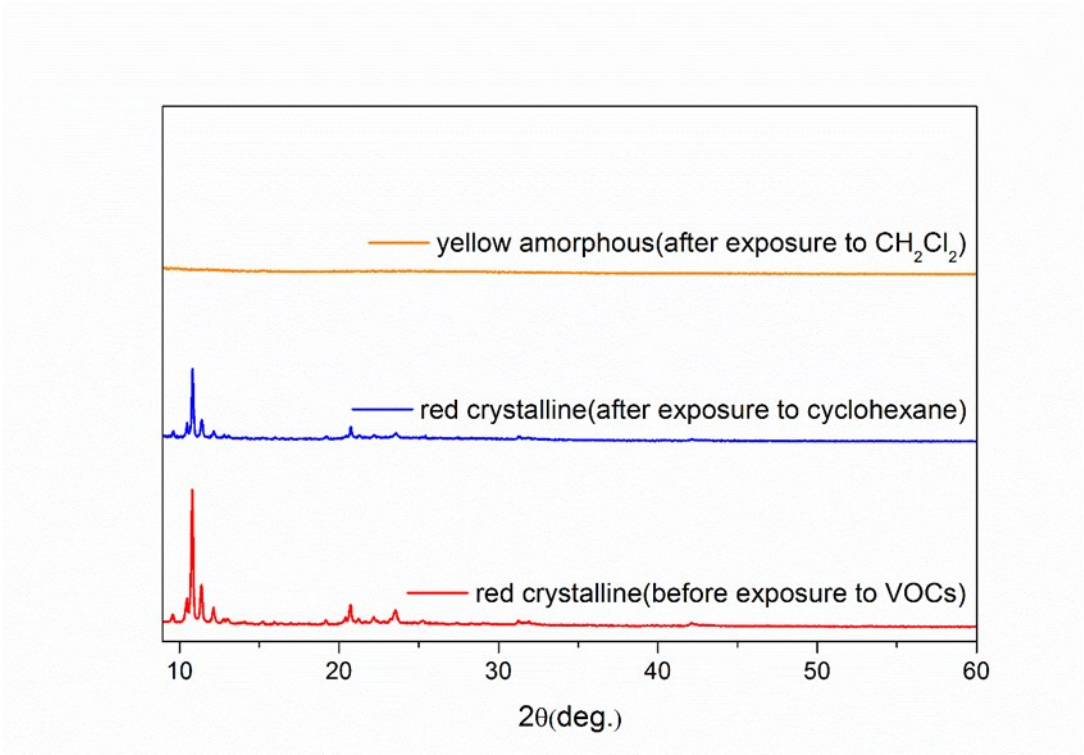
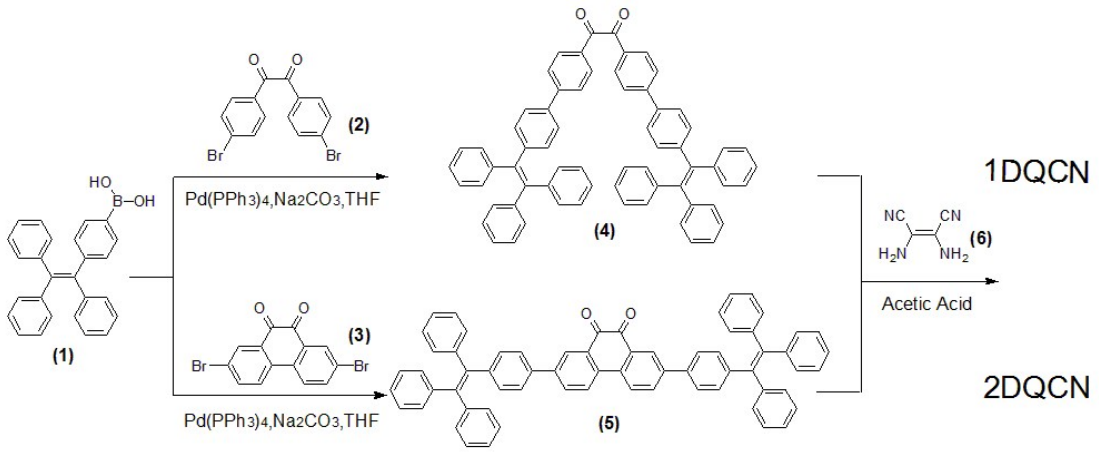


Fig. S7 The XRD patterns of **2DQCN** crystalline films before and after exposure to CH_2Cl_2 and cyclohexane solvents.

8. Synthesis



Scheme 2 Synthetic Routes to **1DQCN** and **2DQCN.**

1DQCN and **2DQCN** are efficiently prepared by a facile two-step approach and the synthetic routes to the two compounds are depicted in **Scheme 2**. 4-(1,2,2-triphenylvinyl)phenylboronic acid **(1)** was prepared by lithiation of 1-(2-(4-bromophenyl)-1,2-diphenylvinyl)benzene, followed by treatment with trimethyl borate and hydrolysis catalyzed by acid according to ref [1]. 1,2-bis(4-bromophenyl)ethane-1,2-dione **(2)**, and 2,7-dibromophenanthrene-9,10-dione **(3)** were prepared according to published methods, [2], [3] and [4]. The other typical procedures for their syntheses are shown below.

1,2-bis(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)ethane-1,2-dione (4) and 2,7-bis(4-(1,2,2-triphenylvinyl)phenyl)phenanthrene-9,10-dione (5): Into a stirred mixture of 0.736 g (2 mmol) of **(2)** (0.732 g (2 mmol) of **(3)**), 1.504 g (4 mmol) of **(1)**, and 12 mL of 2 M Na_2CO_3 solution in 30 mL THF was added 0.02 g of $Pd(PPh_3)_4$ under nitrogen. The mixture was heated to 80℃ for 12 h. After being cooled to room temperature, the solution was extracted with 50 mL of CH_2Cl_2 twice, washed with water, and dried over Na_2SO_4. After filtration and solvent evaporation under reduced pressure, the product was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. The pale yellow solid of **(4)** and orange solid of **(5)** were obtained in 63.3% yield (1.10 g) and 66.2% yield (1.15g), respectively. **(4)** ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.99-8.01 (d, 4H), 7.67-7.69 (d, 4H), 7.37-7.39 (d, 4H), 7.02-7.13 (m, 34H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.10, 144.43, 143.57, 143.55, 143.51, 141.76, 140.16, 137.10, 132.07, 131.61, 131.40, 131.35, 131.33, 130.50, 127.86, 127.81, 127.70, 127.34, 126.71, 126.64, 126.61, 126.56. **(5)** ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.19-8.22 (m, 4H), 8.15 (s, 2H), 8.07-8.09 (d, 2H), 7.70-7.74 (t, 2H), 7.61-7.63 (d, 2H), 7.45-7.50 (m, 6H), 7.04-7.19 (m, 26H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 148.34, 144.97, 143.53, 143.49, 143.46, 141.98, 140.04, 137.05, 136.21, 135.92, 135.83, 132.21, 131.40, 131.39, 131.33, 131.25, 131.22, 130.55, 129.68, 129.64, 127.98, 127.93, 127.86, 127.74, 126.77, 126.72, 126.69, 126.54, 123.98, 122.40.

5,6-bis(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)pyrazine-2,3-dicarbonitrile (1DQCN) and 6,11-bis(4-(1,2,2-triphenylvinyl)phenyl)dibenzo[f,h]quinoxaline-2,3-dicarbonitrile (2DQCN): A suspension of **(4)** (0.871 g, 1 mmol) (0.869 g, 1 mmol of **(5)**) and 2,3-diaminomaleonitrile (0.130 g, 1.2 mmol) in acetic acid (10 ml) was heated to reflux for 6h, during which time a yellow precipitate of **1DQCN** (a red precipitate of **2DQCN**) formed. After filtration, the resulting solid was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. **1DQCN** was formed in a 95.3% yield (0.899 g) and **2DQCN** was formed in a 93.6% yield (0.880 g). **1DQCN** ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.61-7.63 (d, 4H), 7.55-7.57 (d, 4H), 7.35-7.38 (d, 4H), 7.02-7.13 (m, 34H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 144.07, 143.63, 143.57, 143.54, 143.49, 141.66, 140.24, 137.05, 133.92, 132.03, 131.38, 131.36, 131.31, 130.29, 129.50, 127.82, 127.77, 127.69, 127.18, 126.62, 126.59, 126.25. HRMS (MALDI-TOF): m/z 942.299 (M^+, calcd 942.372). Anal. Calcd For $C_{70}H_{46}N_4$: C, 89.14; H, 4.92; N, 5.94. Found: C, 88.96; H, 5.08; N, 5.75. **2DQCN** ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 9.15-9.19 (q, 4H), 8.76 (s, 2H), 8.68-8.70 (d, 2H), 7.93-8.01 (q, 4H), 7.81-7.86 (t, 2H), 7.57-7.60 (d, 4H), 7.05-7.24 (m, 26H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 145.17, 144.57, 143.61, 143.54, 142.78, 141.90, 140.15, 137.54, 133.54, 133.24, 132.70, 132.27, 131.41, 131.33, 130.28, 129.01, 127.91, 127.84, 127.73, 127.61, 127.57, 127.19, 126.83, 126.73, 126.69, 126.07, 123.25, 121.25, 113.91, 113.87. HRMS: m/z 941.61 ($[M+H]^+$, calcd 941.36). Anal. Calcd For $C_{70}H_{44}N_4$: C, 89.33; H, 4.71.; N, 5.95. Found: C, 89.02; H, 4.94; N, 5.80.

9. NMR Spectra of Compound (4), (5), 1DQCN, 2DQCN.

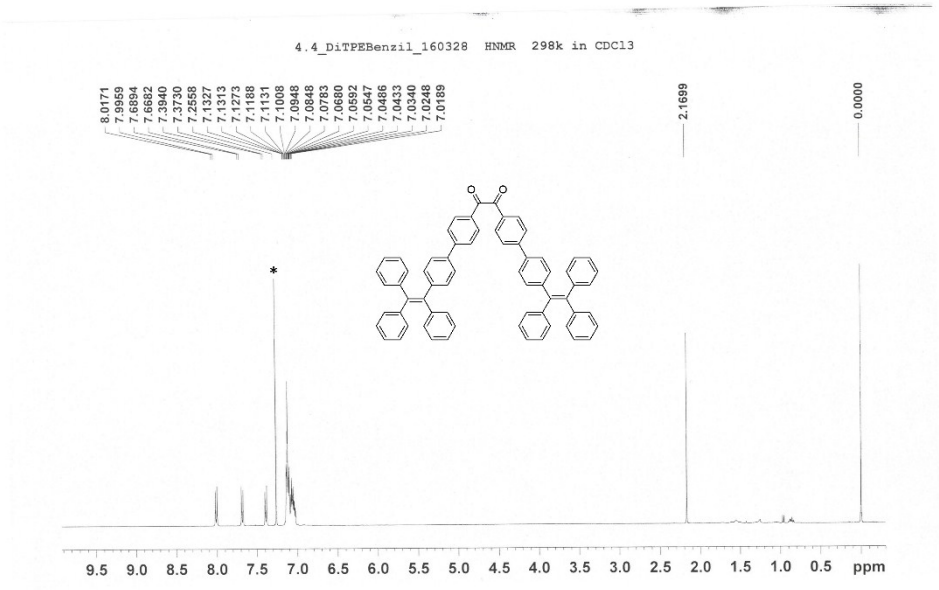


Fig. S8 ^{1}H NMR spectrum of **(4)** in chloroform-*d*. The solvent peaks are marked with asterisks.

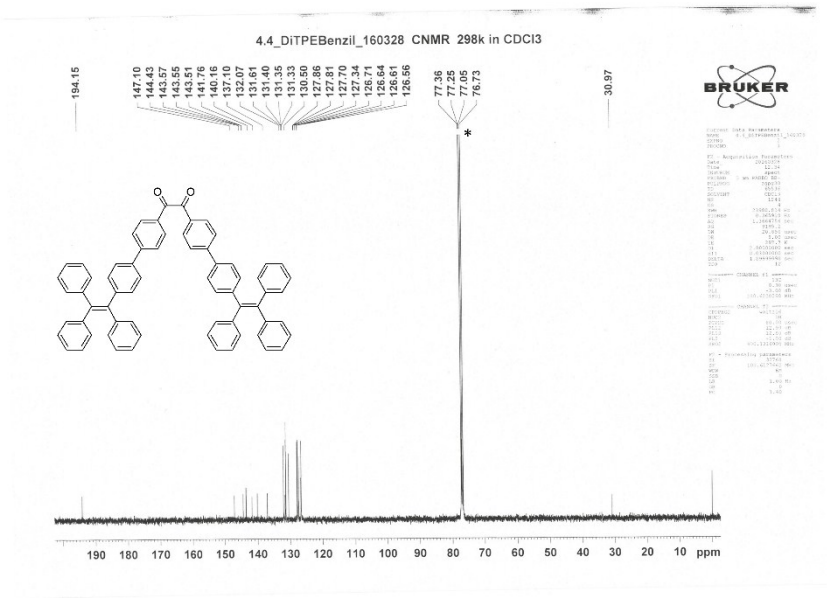


Fig. S9 ^{13}C NMR spectrum of **(4)** in chloroform-*d*. The solvent peaks are marked with asterisks.

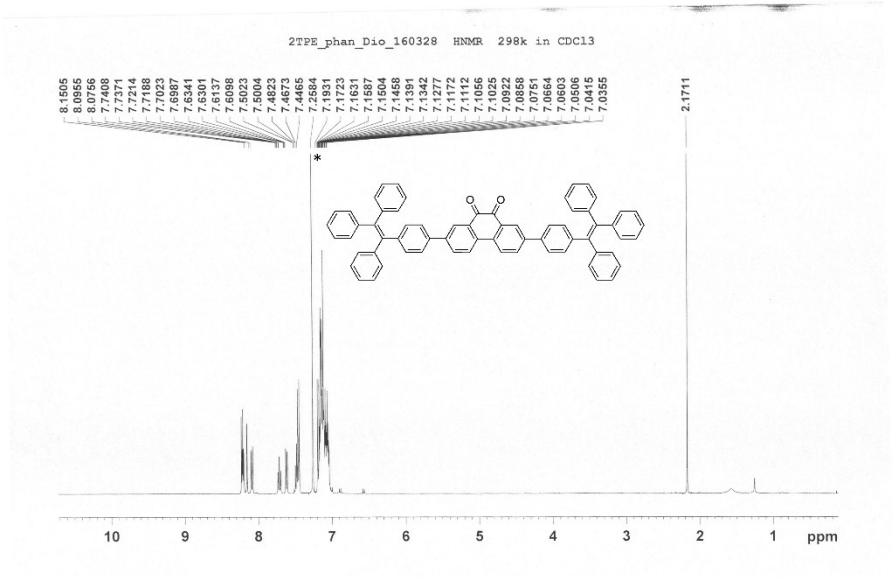


Fig. S10 ^{1}H NMR spectrum of **(5)** in chloroform-*d*. The solvent peaks are marked with asterisks.

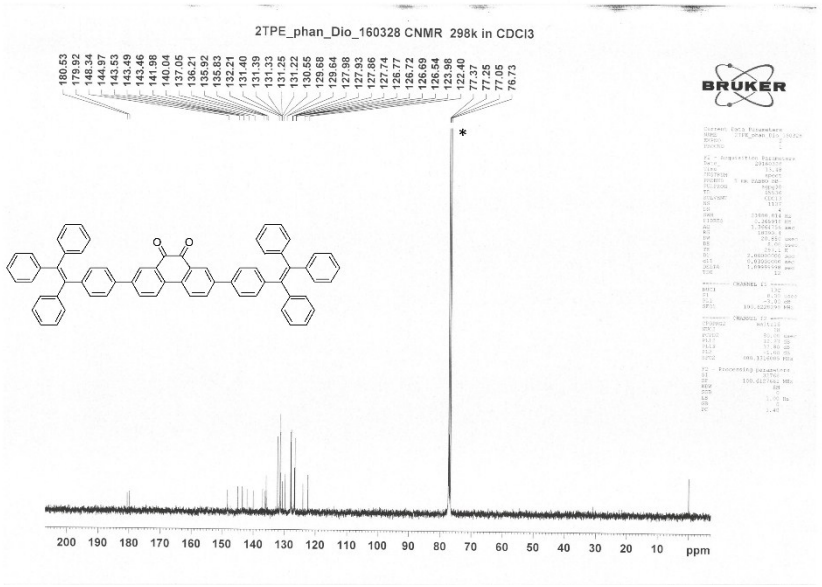


Fig. S11 ^{13}C NMR spectrum of **(5)** in chloroform-*d*. The solvent peaks are marked with asterisks.

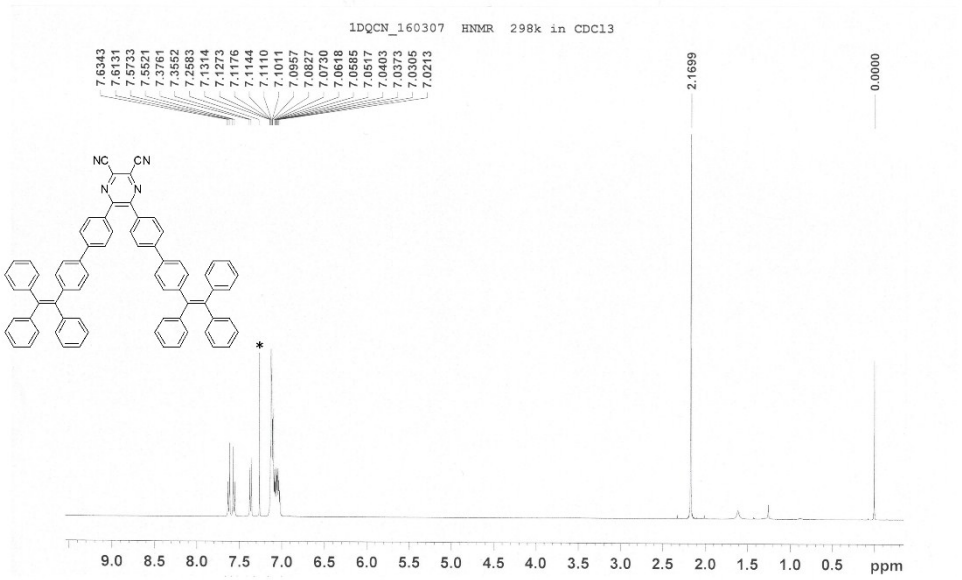


Fig. S12 ^{1}H NMR spectrum of **1DQCN** in chloroform-*d*. The solvent peaks are marked with asterisks.

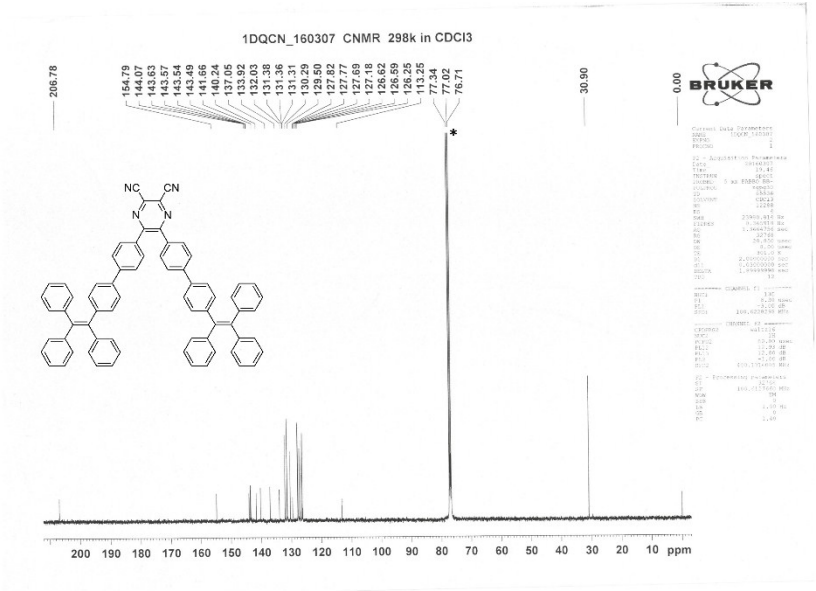


Fig. S13 ^{13}C NMR spectrum of **1DQCN** in chloroform-*d*. The solvent peaks are marked with asterisks.

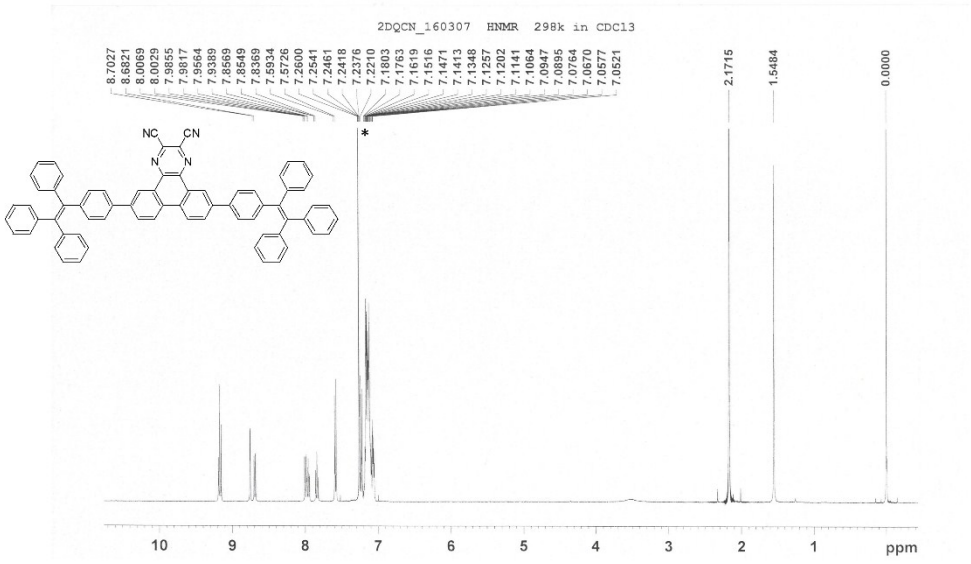


Fig. S14 ^{1}H NMR spectrum of **2DQCN** in chloroform-*d*. The solvent peaks are marked with asterisks.

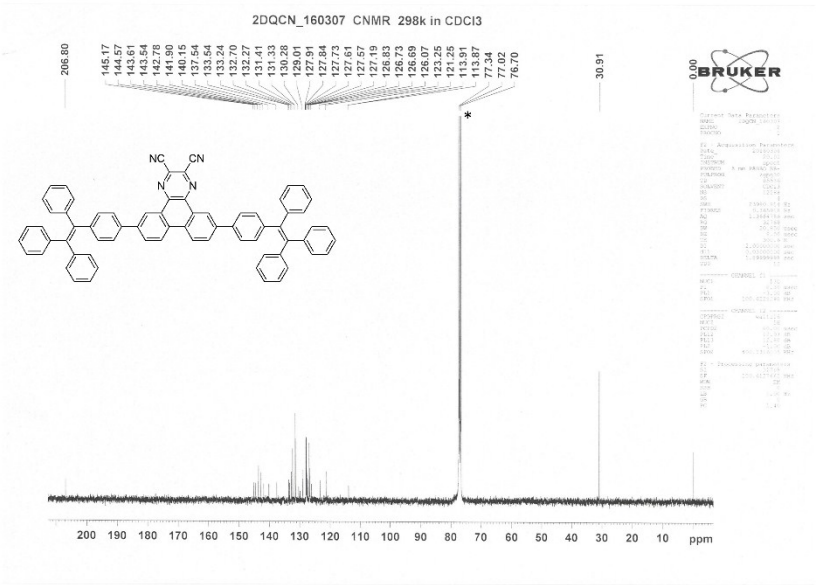


Fig. S15 ^{13}C NMR spectrum of **2DQCN** in chloroform-*d*. The solvent peaks are marked with asterisks.

10. High Resolution Mass Spectra of 1DQCN and 2DQCN.

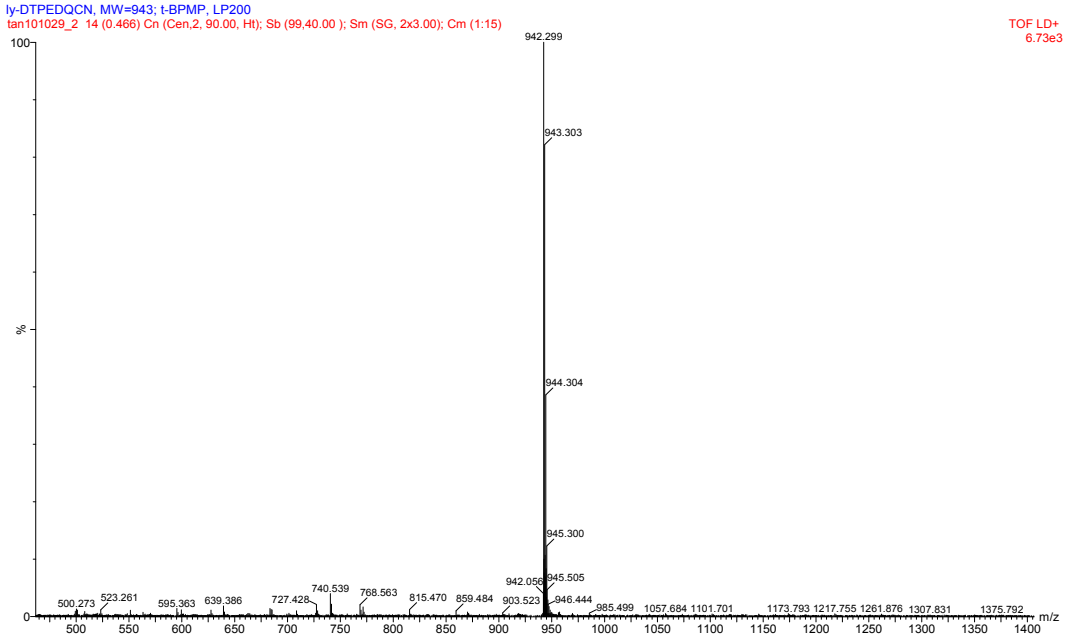


Fig. S16 High resolution mass spectrum of **1DQCN**.

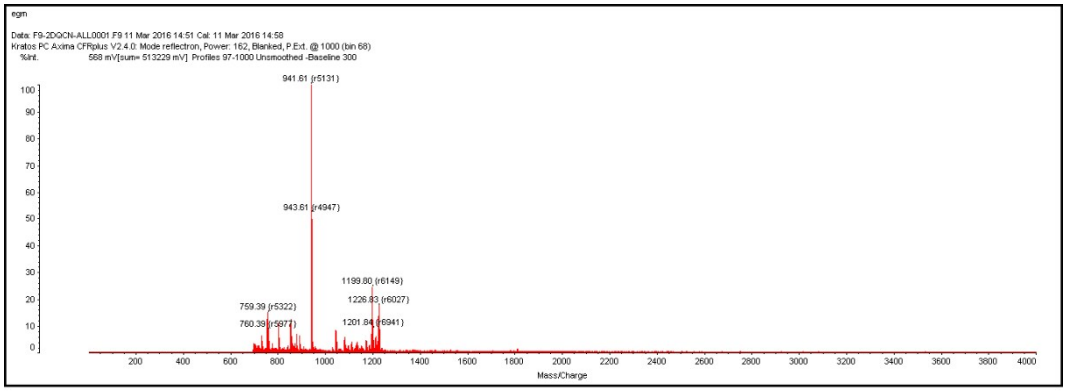


Fig. S17 High resolution mass spectrum of **2DQCN**.

11. Reference

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