Electronic Supplementary Information (ESI)

Aggregation-induced emission enhancement based on 11,11,12,12,-tetracyano-9,10-anthraquinodimethane

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Experimental Section

Materials and Instrumentations

All reagents were used as received from commercial resources unless otherwise specified.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker ADVANCE 400 NMR Spectrometer. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ solvent (77.36 ppm). UV-vis absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Absolute quantum yield measurement (LabSphere®, FluoroMax-4, HORIBA Jobin Yvon, PLQY software package) was used for powder sample. In this experimental setup, it is possible to measure the Photoluminescence Quantum Yields (PLQY) via using the integrating sphere in combination with a commercial fluorimeter. Emission spectrum including the scattering region of excitation light were measured for both blank and test samples, and these spectra were corrected with instrumental factors to calculate the quantum yield.[1]

High-quality single crystals of dP-TCAQ were grown from a CH_2Cl_2/ethanol (1:1) mixture at room temperature. X-ray diffraction intensity data were collected at 173 K on a Saturn724 + CCD diffractometer with graphite monochromated Mo K\α radiation. And the structure and refinement were carried out using the Crystal Clear (Rigaku Inc., 2008).

SEM images were taken by using SEM (Hitachi S-4300 SE).

Synthesis of dP-TCAQ

The dP-TCAQ was prepared according to the synthetic route shown in Scheme 1.

The synthesis of 2,6-diiodoanthracene-9,10-dione was carried out according to a modified procedure from a previously reported synthesis.[2] To a 100 mL flask was added 1.005g start material (4.22 mmol), actonitrile (30 mL) and hydrochloric acid (10 mL 2.4 M), the suspension was cooled to 0 □. Sodium nitrite (10.1 mmol, 694 mg) was dissolved in 2 mL water, then slowing dropped into the former suspension. The whole process was taken at 0 □ in an ice bath. After 30 min stirring, KI (21.4mmol, dissolved in 5 mL water) was added. Then it was allowed to warm up to room temperature, stirring for an hour and then heat to 60 □ for another hour. The crude product was get by filtration, then washed with water and methanol. The filtrate was collected to suspend in CH_2Cl_2(40 mL), filtrated again, washed with CH_2Cl_2, dried in vacuum afford a light brown compound 1.224 g (63% yield). ^{1}H-NMR (400 MHz, 298 K) δ ($CDCl_3$, ppm): 8.64 (s, 2H), 8.17 (d, J = 8 Hz, 2H), 7.98

(d, *J* = 8 Hz, 2H). MS (EI) m/z: 459 (M^+).

2,6-diphenylanthracene-9,10-dione was synthesized by Suzuki coupling reaction. To a 100 mL flask, 460 mg (1 mmol) 2,6-diiodoanthracene-9,10-dione, 268 mg (2.2 mmol) phenylo boric acid and $Pd(PPh_3)_4$ 63 mg (0.05 mmol) was added under argon. Then 8 mL ethanol, 40 mL toluene and 8mL 2M Na_2CO_3aqueous solution was added. The whole system was heated to 90 ℃ and kept for 3 h. The mixture was separated, and the water layer was extracted with CH_2Cl_2 (20 mL × 3), the combined organic layer was dried over anhydrous Na_2SO_4. Solvent was removed under vacuum. Further purification by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (3 : 1) as eluent afforded the product as a yellow solid (260 mg, 72% yield). ^{1}H NMR (400 MHz, 298 K) δ ($CDCl_3$, ppm) 8.58 (d, *J* = 1.7 Hz, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 8.04 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H). MS (EI) m/z: 360 (M^+).

DP-TCAQ was synthesized by $TiCl_4$-mediated Knoevenagel condensation.[3]To a 100 mL flask, 0.5 mmol 2,6-diphenylanthracene-9,10-dione (180 mg), malononitrile (4 mmol, 265 mg) was added under argon , 50 mL chloroform was added as solvent, and it was allowed to reflux at 65 ℃. After the addition of $TiCl_4$ (4 mmol) and pyridine (8 mmol), the whole system was kept at refluxing overnight. Then 50 mL water was added, and separated. The water layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. Solvent was removed under vacuum. Further purification by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (2 : 1) as eluent afforded dP-TCAQ as a bright yellow solid (150 mg, 66% yield). ^{1}H-NMR (400 MHz, 298 K) δ ($CDCl_3$, ppm): 8.48 (d, *J* = 1.6 Hz, 2H), 8.35 (d, *J* = 8.2 Hz, 2H), 7.95 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.71-7.66 (m, 4H), 7.58-7.51 (m, 4H), 7.51-7.45 (m, 2H). ^{13}CNMR (100 MHz, 298K): δ ($CDCl_3$, ppm): ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.35, 134.42, 132.67, 129.61, 129.30, 127.71, 125.94. MS (EI) m/z: 456 (M^+). Anal. calcd for $C_{32}H_{16}N_4$ (%): C: 84.19, H: 3.53, N: 12.27. Found: C: 84.25, H: 3.56, N: 12.37.

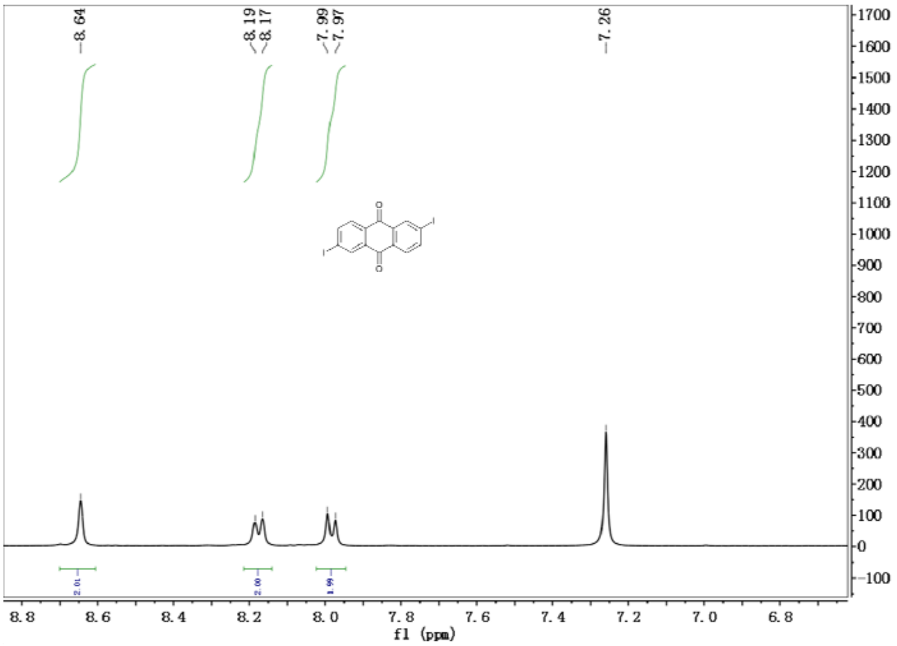
TCAQ was synthesized the same way as dP-TCAQ with a yield of 63%. MS (EI) m/z: 304 (M^+). ^{1}H-NMR (400 MHz, 298 K) δ ($CDCl_3$, ppm): 8.31-8.17 (m, 4H), 7.82-7.65 (m, 4H).

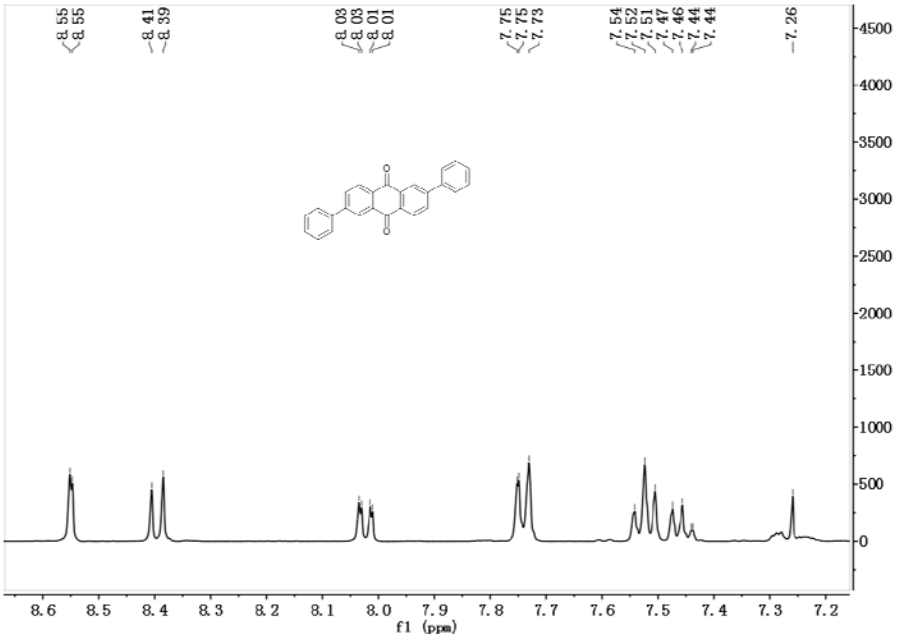
Preparation of aqueous solutions

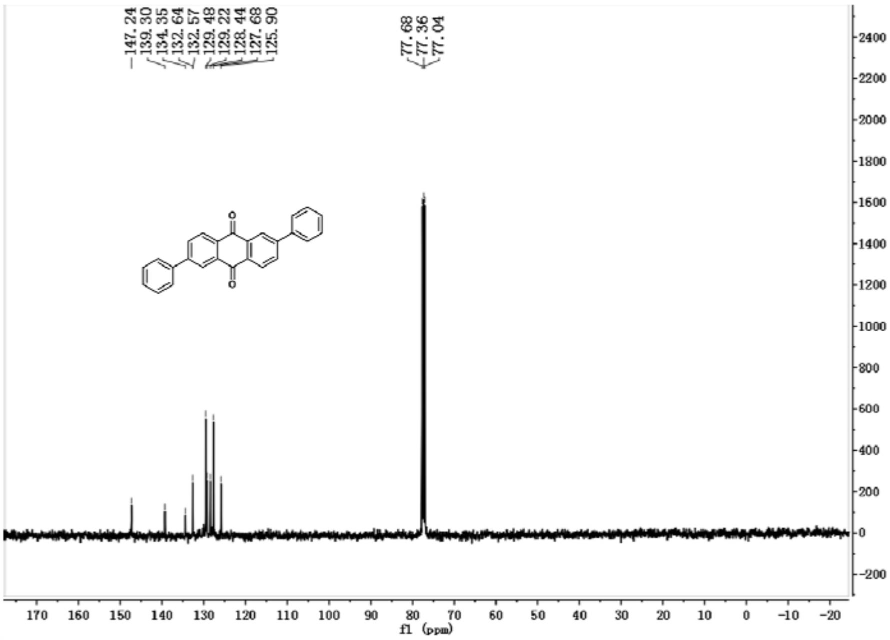
First a solution of dP-TCAQ and TCAQ (10^{-3} M) in acetonitrile was prepared. Then different amount of the solution, acetonitrile and water was mixed to form 2 mL 50 μM solution, and the solution was used for the UV-vis and florescent test.

Preparation of SEM sample

Solutions with certain content of water was first prepared, then a cleaned SiO_2/Si substrate was dipped into the solution and pulled out, the solvent was absorbed away by filtrate paper to avoid further aggregation caused by solvent evaporation.



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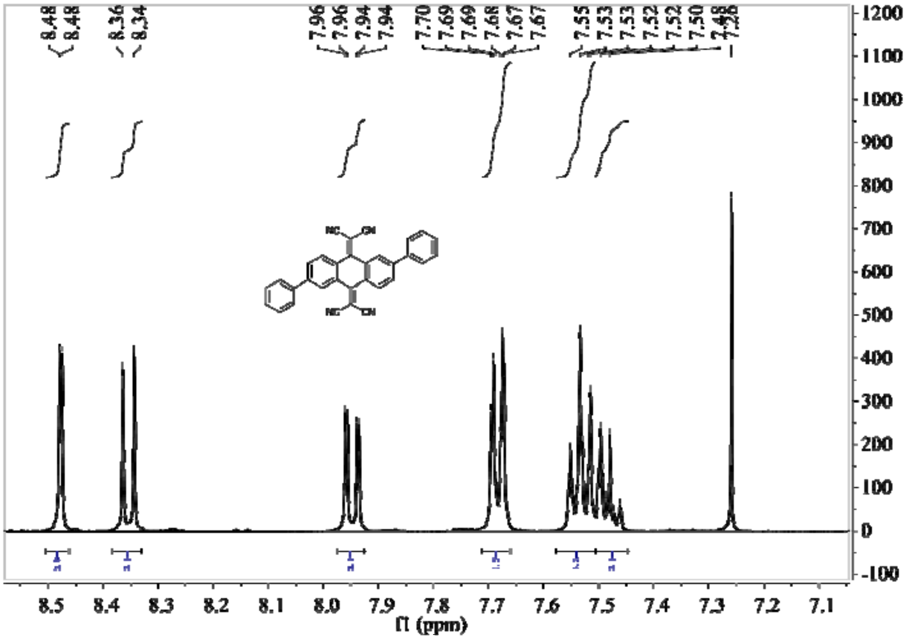
f1 (ppm)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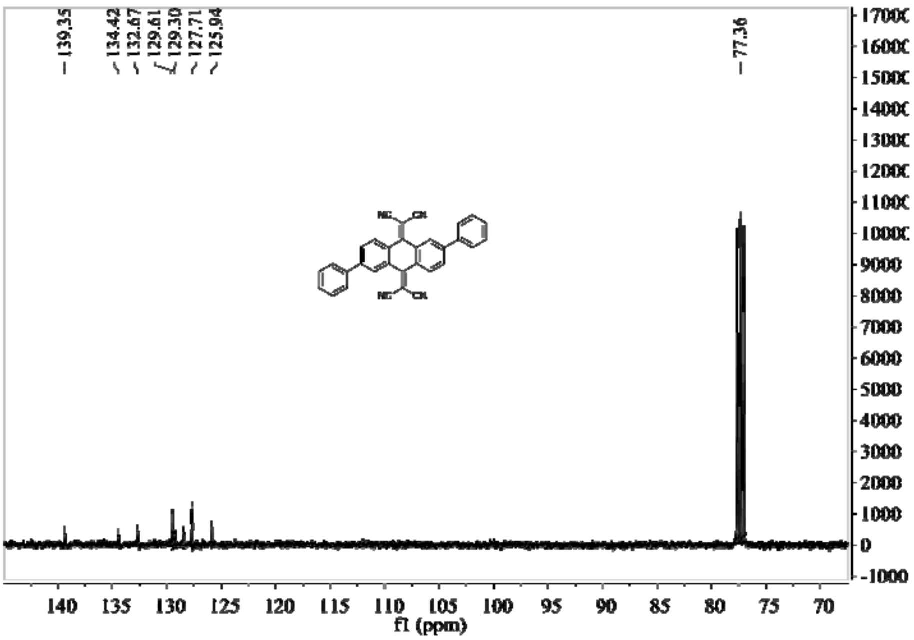

Figure S1. ^{1}H and ^{13}C NMR spectra of the compounds in $CDCl_3$.

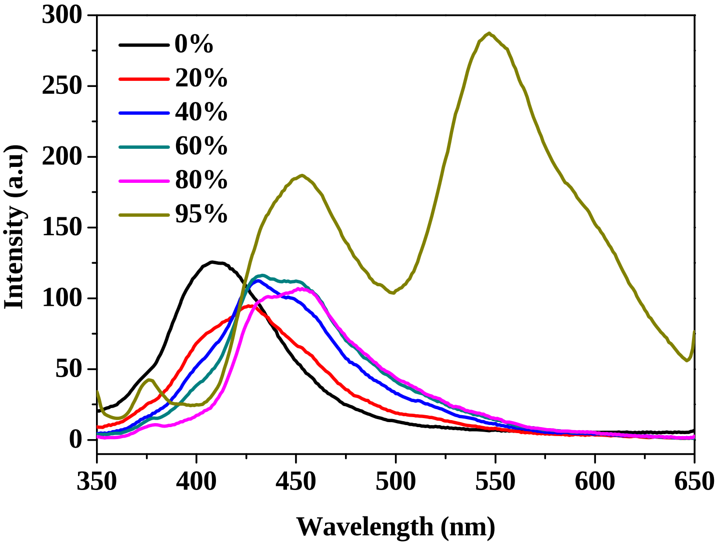

Figure S2. Photoluminescence spectra of TCAQ upon increasing water content, the concentration was kept at 50 μM and excitation wavelength was kept at 340 nm.

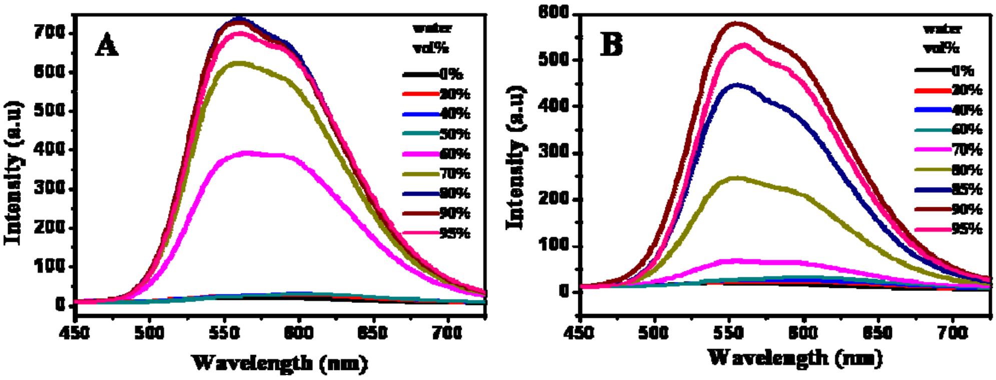

Figure S3. Photoluminescence spectra of dP-TCAQ in different water/solvent (v/v) mixtures. (A) Acetone was used as solvent (concentration: 75 μM), (B) THF was used as solvent (concentration: 100 μM). Excitation wavelength: 380 nm.

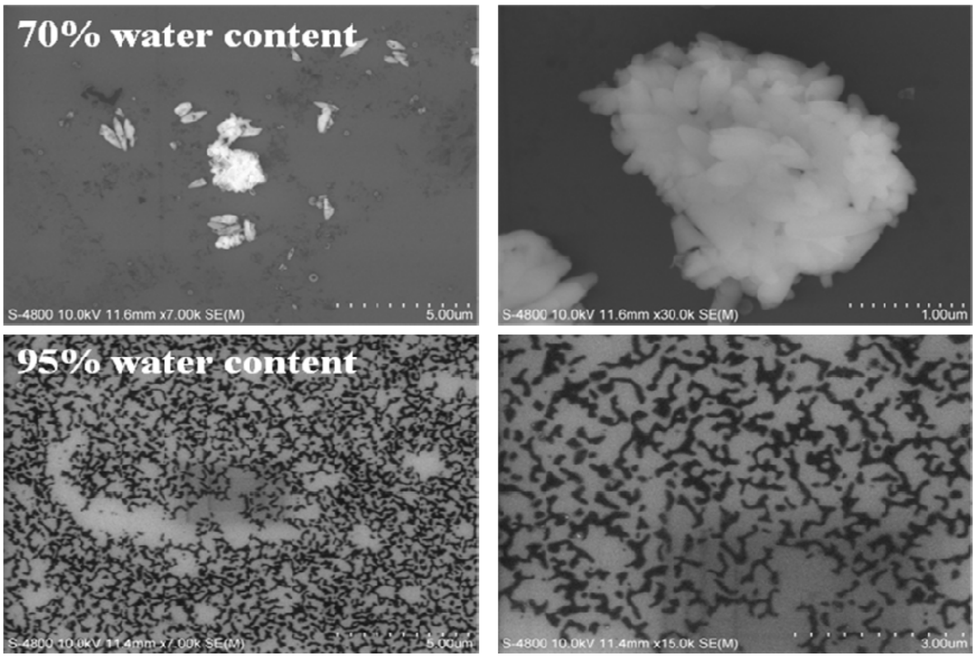

Figure S4. SEM captures of dP-TCAQ aggregates in different aqueous solutions, the right side were enlarged captures of the left ones.

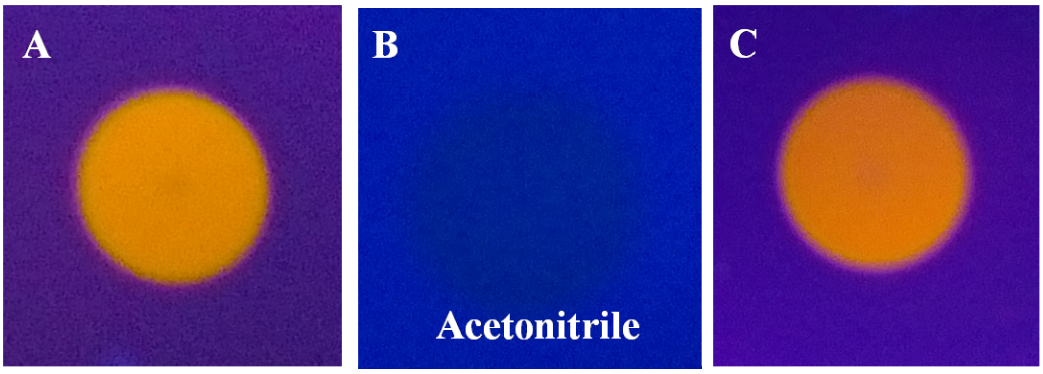

Figure S5. Photos of the spot of dP-TCAQ on the TLC plate (A) without and (B) with saturated acetonitrile vapors. (C) photo of the spots after organic vapor has been evacuated. Same results were get when other solvents (THF, dichloromethane, etc.) were used.

Table S1. Crystal Data and Structure Refinement for *dP-TCAQ* (CCDC 905986)

Empirical formula	C32 H16 N4
Formula weight	456.49
Temperature	173.0 K
Wavelength	0.71073Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 18.945(4) Å □α = 90° b = 9.0720(18) Å □β = 111.45(3)° c = 14.608(3) Å □γ = 90°.
Volume	2336.7(8)Å^3
Z	4
Density (calculated)	1.298 mg/m^3
Absorption coefficient	0.078 mm^{-1}
F(000)	944
Crystal size	0.32 × 0.30 × 0.19 mm^3
Theta range for data collection	2.2450 to 26.0215°
Index ranges	-23<=h<=23, -10<=k<=11, -18<=l<=16
Reflections collected	18061
Independent reflections	4575 [R(int) = 0.0554]
Completeness to theta = 26.02°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7876
Refinement method Full-matrix least-squares on F2	
Data / restraints / parameters	4575 / 0 / 325
Goodness-of-fit on F2	1.377
Final R indices [I>2sigma(I)]	R1 = 0.0980, wR2 = 0.2497
R indices (all data)	R1 = 0.1089, wR2 = 0.2588
Largest diff. peak and hole	0.252 and -0.262 e.Å^{-3}

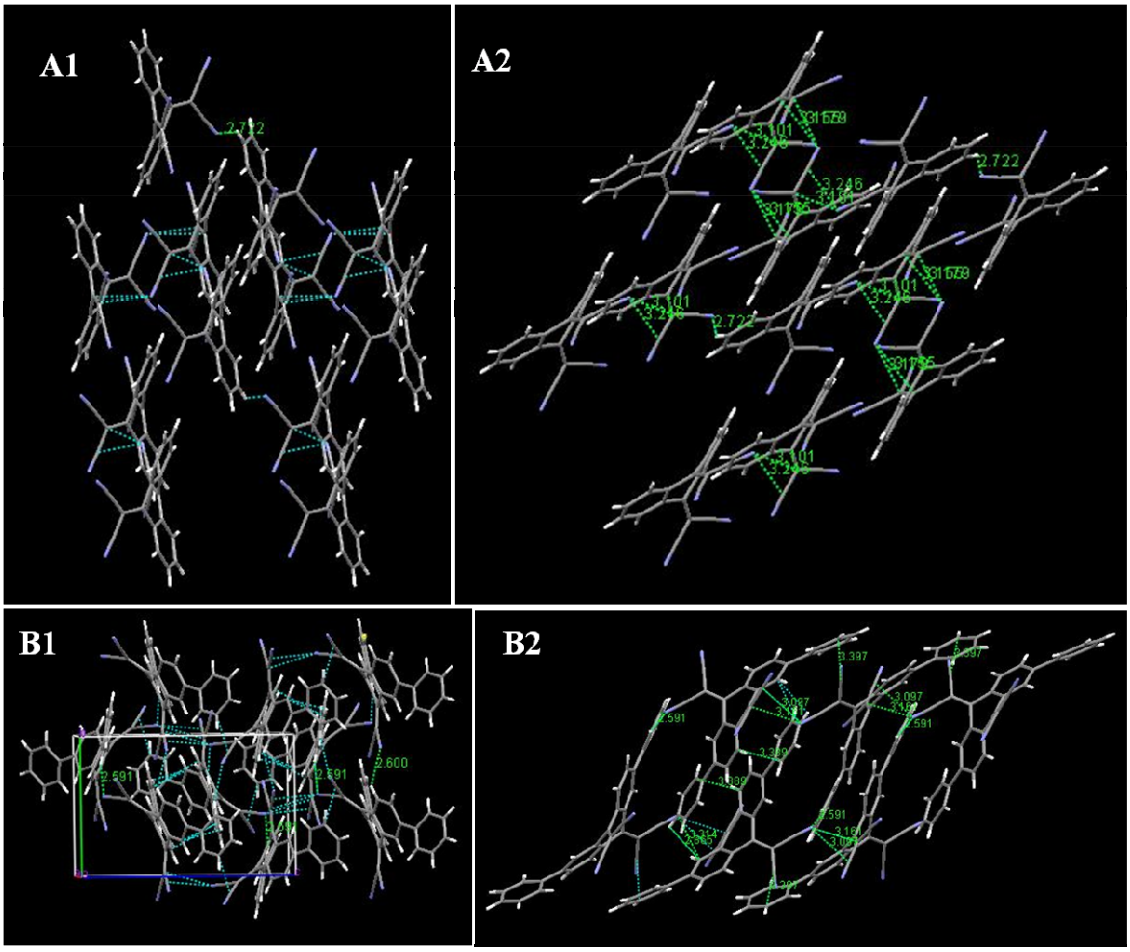

Figure S6. Hydrogen bond (A1) and short contacts (A2) of TCAQ. Hydrogen bond (B1) and short contacts (B2) of dP-TCAQ.

Reference

1. X. Cao, S. Bai; Y. Wu; Q. Liao; Q. Shi; H. Fu, *Chem. Commun.*, 2012, 48, 6402–6404.

2. M. T. S. a. H. L. Anderson, *Chem. Commun.*, 2007, 2387-2389.

3. F. Bureš, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Eur. J. Org. Chem.*, 2008, 994-1004.