Electronic Supplementary Material (ESI) for Chemical Communications

Supplemental Information

For

A Donor-Acceptor-Donor Conjugated Molecule: Twist Intramolecular Charge Transfer and Piezochromic Luminescent Property

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Content

1. Photophysical and DSC measurements

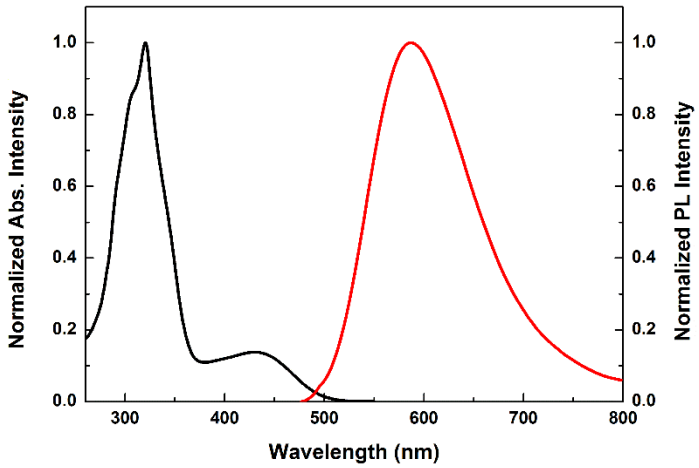


Figure S1. Absorption and emission spectra of **AQDBD** in dilute CH_2Cl_2 solution (10^{-5} M).

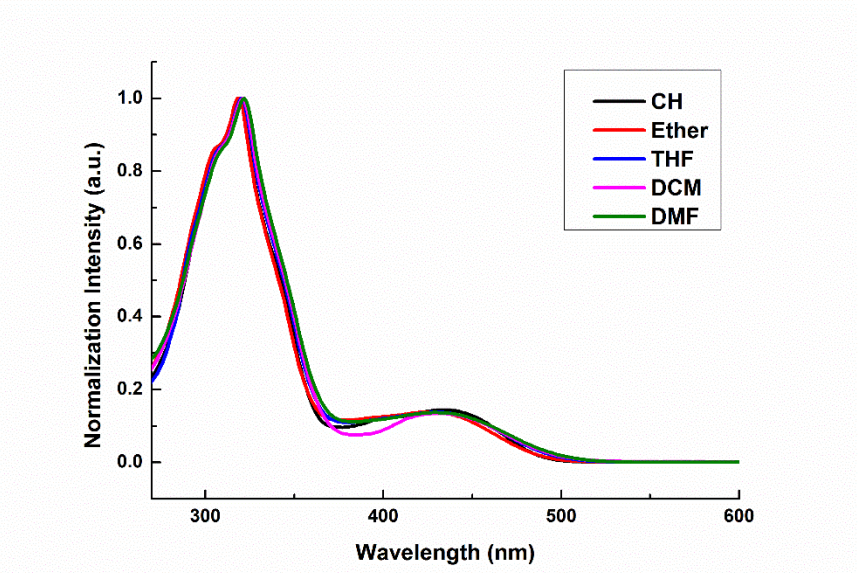


Figure S2. Absorption spectra of **AQDBD** in different solvents (10^{-5} M), varying from cyclohexane to DMF in the sequence of permittivity. (CH: cyclohexane; Ether: diethyl ether; THF: tetrahydrofuran; DCM: dichloromethane; DMF: dimethylformamide)

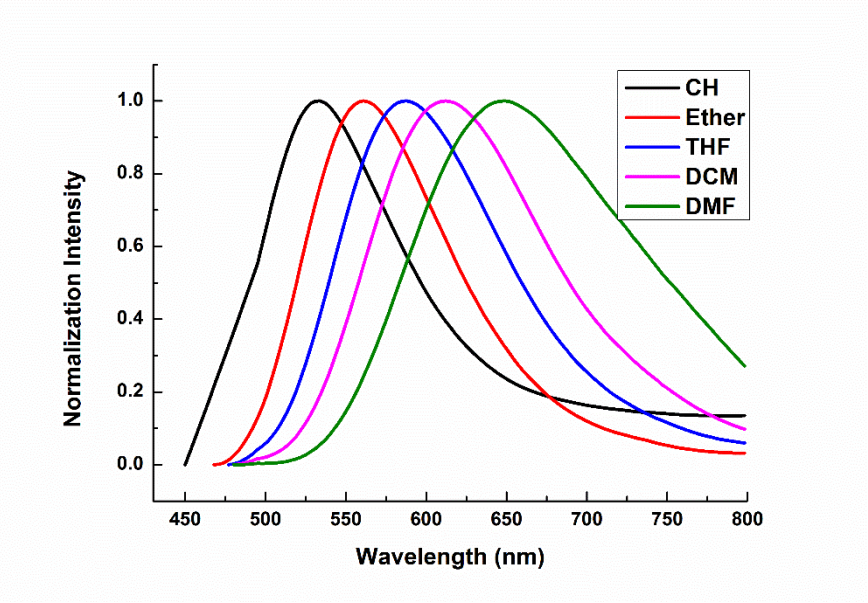


Figure S3. Emission spectra of **AQDBD** in different solvents (10^{-5} M), varying from cyclohexane to DMF in the sequence of permittivity.

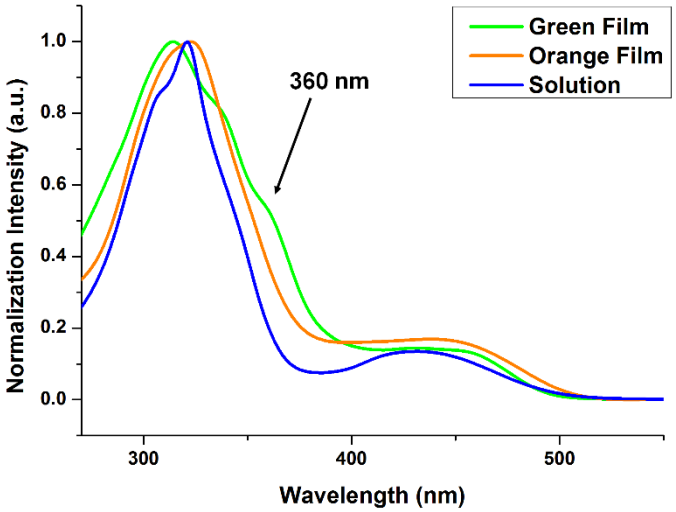


Figure S4. Absorption spectra of green, orange films, and solution of **AQDBD**.

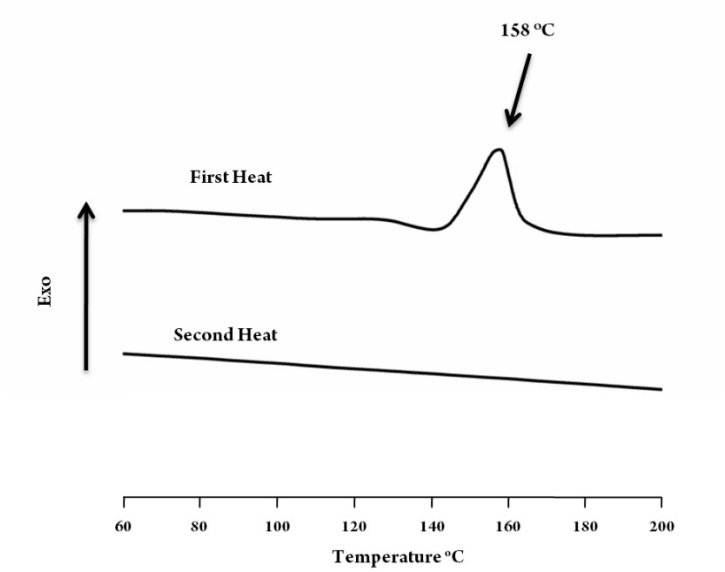


Figure S5. DSC profile of **AQDBD** with an exothermic peak in the first cycling.

Table S1. Optical property of **AQDBD** in different solvent.

	CH	Tol	THF	DCM	Acetone	DMF	DMSO	CH_3CN
η (%)[a]	60	49	41	31	18	10	7	3
λ_{em} (nm)	522	541	570	590	596	600	609	605
ε[b]	2.10	2.38	7.35	9.14	21.4	36.7	45.0	38.8

[a] The fluorescence quantum yields in different solvents was test by integrating sphere system on HORIBA JobinYvon Nanolog FL3-2iHR spectrometer. [b] The permittivity of different solvents.

2. Reversible switching of the emission

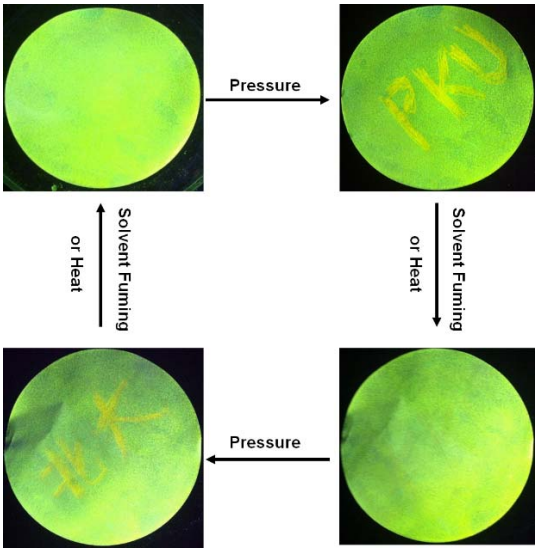


Figure S6. Reversible switching of the emission color of **AQDBD** on filter paper.

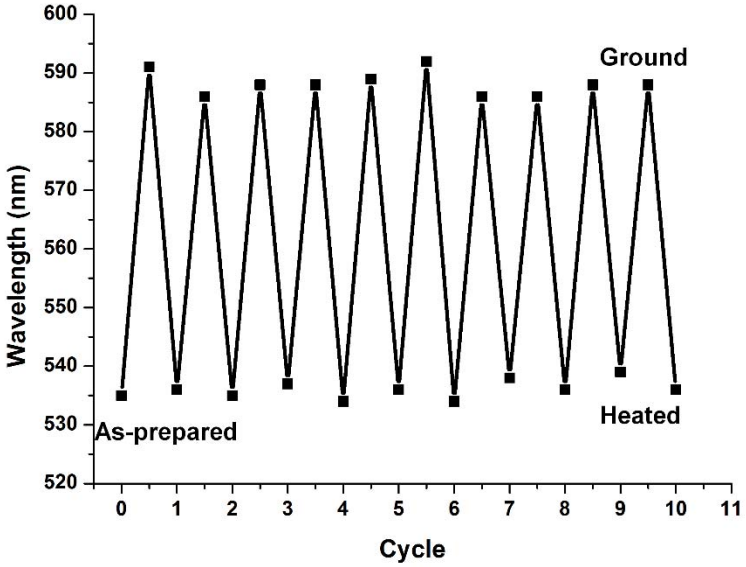


Figure S7. Emission wavelengths of the repeated conversion between the ground and after heated at 160 for 5 min of **AQDBD**.

3. DFT calculation

Atomic structures of **AQDBD** were optimized with density functional theory (DFT) calculations using B3LYP/6-31G at different twist angles from 0° to 180° between TPA and acceptor core with a step length of 10°. Two TPA donors were in cross fashion which have lower ground state energy compared to parallel one at different twist angles. Molecular orbital shapes and energies were calculated at the optimized geometries. Orbital pictures were generated with Gaussview 5.0. All quantum-chemical calculations were performed with the Gaussian09 package.

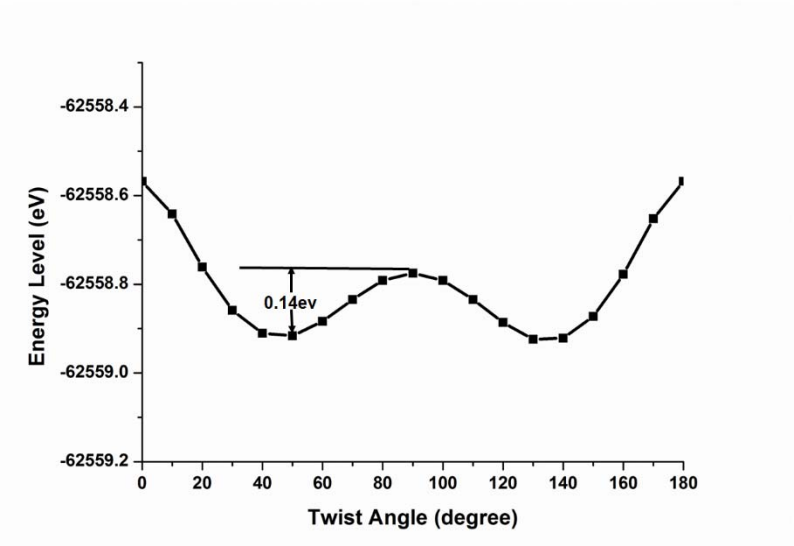
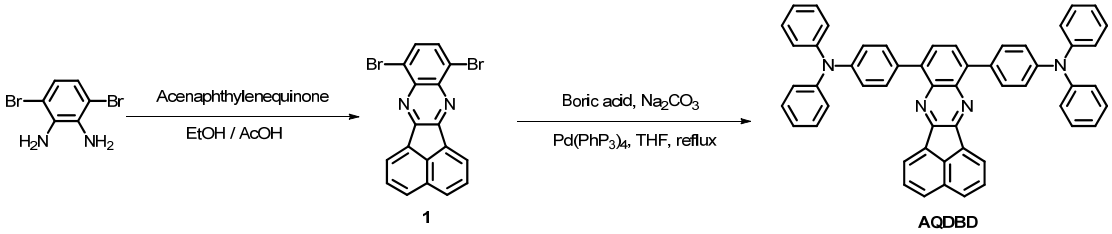


Figure S8. The ground state energy of **AQDBD** at different twist angles between donor and acceptor in the gas phase

4. Synthetic part



Scheme S1. The synthetic routes to **AQDBD**.

8,11-Dibromoacenaphtho[1,2-b]quinoxaline (1). A mixture of 3,6-dibromobenzene-1,2-diamine (53 mg, 0.2 mmol), acenaphthylenequinone (54 mg, 0.3 mmol), and acetic acid (1 mL) were refluxed in ethanol (20 ml) overnight under nitrogen atmosphere. After removal of ethanol under reduced pressure, the residue was dissolved in CH_2Cl_2. The mixture was washed with water, and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was further purified by column chromatography (silica gel, PE:CH_2Cl_2 = 1:2) to give **1** as a yellow solid (72 mg). Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.57-8.55 (d, J = 7.0 Hz, 2H), 8.18-8.16 (d, J = 8.2 Hz, 2H), 7.93 (s, 2H), 7.91 –7.87 (t, J = 7.6 Hz, 2H).

4,4'-(Acenaphtho[1,2-b]quinoxaline-8,11-diyl)bis(*N*,*N*-diphenylaniline) (AQDBD). To a mixture of **1** (82 mg, 0.2 mmol), (4-(diphenylamino)phenyl)boronic acid (144 mg, 0.5 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), and sodium carbonate (170 mg, 1.61 mmol) were added THF (40 mL) and water (10 mL). The mixture was refluxed overnight under nitrogen atmosphere. After quenched with aqueous NH_4Cl solution, the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography (silica gel, PE : $CHCl_3$ = 1 : 1) to afford **AQBDB** as a yellow solid (123 mg). Yield: 83%. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, ppm): δ 8.39-8.38 (d, J = 7.0 Hz, 2H), 8.15-8.13 (d, J = 8.2 Hz, 2H), 7.91–7.84 (m, 8H), 7.38–7.28 (m, 20H), 7.13-7.10 (t, J = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $C_2Cl_4D_2$, ppm): δ 152.9, 147.7, 147.3, 139.3, 139.2, 136.7, 132.5, 132.2, 132.2, 130.1, 129.8, 129.7, 129.6, 128.9, 124.9, 123.3, 122.8, 122.2. EI-HRMS: Calcd. for $[M + H]^+$: 741.3013. Found: 741.3005.