Supplemental Information

For

A Donor-Acceptor-Donor Conjugated Molecule: Twist

Intramolecular Charge Transfer and Piezochromic Luminescent Property

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1. Photophysical and DSC measurements

**Figure S1.** Absorption and emission spectra of AQDBD in dilute CH$_2$Cl$_2$ 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.

<table>
<thead>
<tr>
<th></th>
<th>CH</th>
<th>Tol</th>
<th>THF</th>
<th>DCM</th>
<th>Acetone</th>
<th>DMF</th>
<th>DMSO</th>
<th>CH₃CN</th>
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<tbody>
<tr>
<td>η (%)⁴</td>
<td>60</td>
<td>49</td>
<td>41</td>
<td>31</td>
<td>18</td>
<td>10</td>
<td>7</td>
<td>3</td>
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<tr>
<td>λₑₓ (nm)</td>
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<td>541</td>
<td>570</td>
<td>590</td>
<td>596</td>
<td>600</td>
<td>609</td>
<td>605</td>
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<tr>
<td>ε⁵</td>
<td>2.10</td>
<td>2.38</td>
<td>7.35</td>
<td>9.14</td>
<td>21.4</td>
<td>36.7</td>
<td>45.0</td>
<td>38.8</td>
</tr>
</tbody>
</table>

⁴ The fluorescence quantum yields in different solvents was test by integrating sphere system on HORIBA JobinYvon Nanolog FL3-2iHR spectrometer. ⁵ 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

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 CH₂Cl₂. The mixture was washed with water, and then dried over anhydrous Na₂SO₄. After removal of the solvent under reduced pressure, the residue was further purified by column chromatography (silica gel, PE:CH₂Cl₂ = 1:2) to give 1 as a yellow solid (72 mg). Yield: 87%. ¹H NMR (400 MHz, CDCl₃, 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(PPh₃)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 NH₄Cl solution, the mixture was extracted with CH₂Cl₂. The combined organic extracts were washed with brine and dried over anhydrous Na₂SO₄. After removal of the solvents under reduced pressure, the residue was purified by column chromatography (silica gel, PE : CHCl₃ = 1 : 1) to afford AQDBD as a yellow solid (123 mg). Yield: 83%. ¹H NMR (400 MHz, C₂D₂Cl₄, 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). ¹³C NMR (100 MHz, C₂Cl₄D₂, 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. El-HRMS: Caled. for [M + H]⁺: 741.3013. Found: 741.3005.