Supporting Information

Role of voluminous substituents in controlling optical properties of disc/planar-like small organic molecules: Toward molecular emission in solid state

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Scheme S1. Complete synthesis scheme utilized to obtain BC-CY6 and BC-LTH.
**Synthesis of compound 1a**

Lithocholic acid was dissolved in pyridine and followed by the addition of acetic anhydride over continuous stirring. The reaction mixture was stirred for 6 hrs and then poured over the cold water (100 ml) containing 5 % hydrochloric acid and allowed to stand for 2 hours. The white precipitates were then collected, washed with water and dried in hot oven at 60 °C for 12 hours. The white powder was collected as pure product and used for further reaction.

Obtained white powder was dissolved in THF solution and one drop of N,N-Dimethylmethanamide (DMF) as catalyst was added to the solution under nitrogen atmosphere. The reaction mixture was then brought to 0°C and added slowly with thionyl chloride and then refluxed for 5 hours. After refluxing, the reaction mixture was dried over vacuum at 80 °C to remove excess thionyl chloride. The cream coloured powder was then used as it is without any purification.

**Synthesis of BC-CY6**

The coumarin derivative BC-OH was dispersed in dichloromethane and added with triethylamine at 0 °C followed by the addition of cyclohexanecarbonyl chloride at the same temperature. The reaction mixture was then stirred at room temperature for 6 hours. After the completion of the reaction, the reaction was quenched with the addition of water (10 mL) and extracted with excess dichloromethane. The organic layer was then washed with excess of water (10 mL X 3) and dried over sodium sulfate. The organic layer was then concentrated under vacuum to obtain yellowish green powder which was then washed with hexane and diethyl ether to obtain pure product.
Yellow solid, M. P. - 238°C. \(^1\)H-NMR (CDCl\(_3\)-d\(_1\), 500 MHz, \(\delta\)) : 8.64 (d, \(J = 8.9\) Hz, 1H), 7.66-7.64 (m, 4H), 7.6 (d, \(J = 8.9\) Hz, 1H), 7.54-7.52 (m, 2H), 7.46-7.44 (m, 1H), 7.32 (d, \(J = 8.9\) Hz, 1H), 2.7-2.6 (m, 1H), 2.13-2.10 (m, 2H), 1.74-1.7 (m, 1H), 1.7-1.6 (m, 2H), 1.4-1.3 (m, 3H).

\(^13\)C-NMR (CDCl\(_3\)-d\(_1\), 125 MHz, \(\delta\)) 174.0, 164.6, 157.2, 152.5, 152.3, 137.2, 132.1, 131.0, 129.2, 128.4, 125.1, 124.7, 123.6, 123.3, 120.4, 118.9, 113.7, 100.4, 42.2, 28.9, 25.6, 25.2. FTIR (KBr, cm\(^{-1}\)) : 701.3, 757, 807, 904.6, 908.2, 960, 1014.1, 1099.6, 1143.8, 1234.7, 1357.6, 1397.7, 1473.7, 1584.8, 1628.4, 1725.8, 2231.8, 2855.8, 2935.6, 3070.07. HRMS: m/z calculated for C\(_{27}\)H\(_{21}\)NO\(_4\) [M+Na] 446.1368, found 446.1363.

**Synthesis of BC-LTH**

The coumarin derivative BC-OH was dispersed in dichloromethane and added with triethylamine at 0 °C followed by the addition of compound 1a at the same temperature. The reaction mixture was then stirred at room temperature for 6 hours. After the completion of the reaction, the reaction was quenched with the addition of water (10 ml) and extracted with excess dichloromethane. The organic layer was then washed with excess of water (10 ml X 3) and dried over sodium sulfate. The organic layer was then concentrated under vacuum to obtain yellow powder which was then washed with hexane and diethyl ether to obtain pure product

Pale yellow solid, M.P- 176°C. \(^1\)H-NMR (CDCl\(_3\)-d\(_1\), 500 MHz, \(\delta\)) : 8.6 (d, \(J = 9.6\) Hz, 1H), 7.66-7.63 (m, 4H), 7.61 (d, \(J = 8.9\) Hz, 1H), 7.53-7.50 (m, 2H), 7.47-7.45 (m, 1H), 7.31 (d, \(J = 8.9\) Hz, 1H), 4.75-4.70 (m, 2H), 2.7-2.6 (m, 1H), 2.6-2.54 (m, 1H), 2.01 (s, 3H), 2.0-1.8 (m, 6H), 1.7-1.3 (m, 12H), 1.2-1.0 (m, 5H), 1.0-0.9 (m, 6H), 0.7-0.6 (m, 4H). \(^13\)C-NMR (CDCl\(_3\)-d\(_1\), 125 MHz, \(\delta\)) 172.3, 170.6, 164.6, 157.1, 152.3, 137.2, 132.1, 131.1, 129.2, 128.4, 125.2, 124.8, 123.6, 123.2, 120.5, 118.9, 113.7, 113.4, 100.5, 74.3, 56.5, 55.9, 42.7, 41.8, 40.3, 40.1, 35.7,
35.4, 35.3, 35.0, 34.0, 32.2, 31.4, 30.8, 29.6, 28.2, 28.1, 26.9, 26.6, 26.3, 24.1, 23.3, 21.4, 20.8, 18.3, 12.0. FTIR (KBr, cm\(^{-1}\)): 700.1, 755.6, 821.5, 902.5, 926.3, 1025.7, 1092.1, 1152.5, 1242.1, 1359.1, 1584.6, 1628.9, 1733.8, 2227.4, 2856.6, 2926.3. HRMS: m/z calculated for C\(_{46}H_{51}NO_6\) [M+Na] 736.3614, found 736.3601.
Figure S1. Solvatochromic effect on UV-vis absorption and photoluminescence (PL) profiles for BC-CY6 (a,b) and BC-LTH (c,d). The UV-vis absorption (e) and PL (f) profiles for coumarin Bc-OH for comparison.
Figure S2. DLS data for the compounds BC-CY6 and BC-LTH before and after addition of water into THF solution of respective dyes.
Figure S3. ORTEP diagram of crystal structure of BC-CY6. The trapped dichloromethane solvent is also shown.
Figure S4. Torsional angle (46.6°) between plane of phenyl ring and plane of naphthalene ring in BC-CY6 (Inset: image of crystals under day light (left) and UV lamp (right: 365 nm lamp) (a), intermolecular short range contacts exhibited by BC-CY6 (b).
Figure S5. Image showing the π-π overlapping in two packed molecules of BC-CY6.

Figure S6. Face to face stacked molecules with intermolecular distance (a) and space-fill image (b) of BC-CY6 from SC-XRD data.
Figure S7. Optimized geometry of observed dimer like configuration in BC-CY6.

Figure S8. TD-DFT simulated UV-vis spectra for BC-CY6 along with the involved orbitals.
Figure S9. TD-DFT simulated UV-vis spectra for BC-LTH along with the involved orbitals.
Table S1. Photophysical data for BC-CY6 and BC-LTH.

| Compound | PL maxima($\lambda_{ex}$) (nm) | Quantum Yield (solution)* | Quantum Yield (solid)* | Lifetime (ns) | Average Lifetime (ns) |
|----------|--------------------------------|--------------------------|------------------------|--------------|-----------------------|
|          |                                |                          |                        | $\tau_1$     | $\tau_2$              |
| BC-CY6   | 460 (341)                      | 29%                      | 14%                    | 0.4 (86%)    | 1.8 (14%)             | 0.6                   |
| BC-LTH   | 460 (341)                      | 30%                      | 23%                    | 0.5 (83%)    | 1.7 (17%)             | 0.7                   |

*Absolute quantum yield. In lifetime column, corresponding contribution for each component have been given in braces.

Figure S10. Relative sizes of the side substituents on the BC-CY6 (a) and BC-LTH (b).
Table S2. Crystal data and structure refinement for BC-CY6.

| BC-CY6          |                          |
|-----------------|--------------------------|
| Identification code | BCHEX_RT_CU              |
| Empirical formula | C_{28}H_{23}Cl_{2}NO_{4} |
| Formula weight   | 508.37                   |
| Temperature/K    | 293(2)                   |
| Crystal system   | triclinic                |
| Space group      | P-1                      |
| a/Å              | 9.2475(6)                |
| b/Å              | 9.4204(6)                |
| c/Å              | 15.7622(9)               |
| α/°              | 80.174(5)                |
| β/°              | 88.298(5)                |
| γ/°              | 66.777(6)                |
| Volume/Å³        | 1242.28(13)              |
| Z                | 2                        |
| ρ calc g/cm³     | 1.359                    |
| μ/mm⁻¹           | 2.641                    |
| F(000)           | 528.0                    |
| Crystal size/mm³ | 0.377 × 0.202 × 0.089    |
| Radiation        | CuKα (λ = 1.54184)       |
| 2Θ range for data collection/° | 10.38 to 133.86 |
| Index ranges     | -10 ≤ h ≤ 11, -11 ≤ k ≤ 8, -18 ≤ l ≤ 18 |
| Reflections collected | 7300                  |
| Independent reflections | 4338 [R_int = 0.0265, R_sigma = 0.0381] |
| Data/restraints/parameters | 4338/0/316             |
| Goodness-of-fit on F² | 1.074                   |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0751, wR₂ = 0.2078 |
| Final R indexes [all data] | R₁ = 0.0847, wR₂ = 0.2205 |
| Largest diff. peak/hole / e Å⁻³ | 0.83/-0.57         |
Figure S11. $^1$H-NMR spectrum of BC-LTH
Figure S12. $^{13}$C-NMR spectrum of BC-LTH
Figure S13. $^1$H-NMR spectrum of BC-CY6
Figure S14. $^{13}$C-NMR spectrum of BC-CY6