Electronic Supplementary Material (ESI) for RSC Advances.

Packing Directed Beneficial Role of 3-D Rigid Alicyclic Arms on Templated Molecular Aggregation Problem

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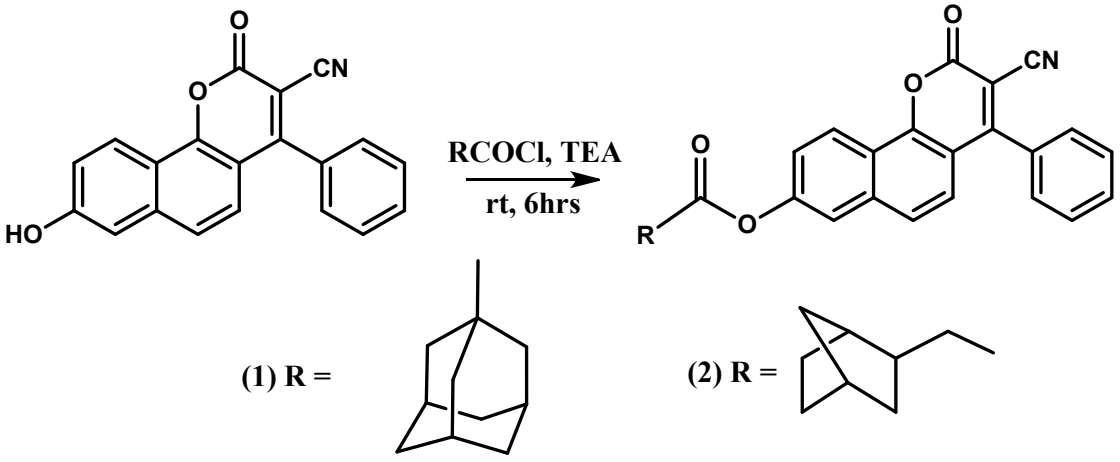
Synthesis.



Scheme S1. Synthesis pathway to compound **1** and compound **2**.

Compound 1. To a dichloromethane suspension of hydroxyl coumarin (1eq) was added triethylamine (2.5 eq) followed by the addition of 1-adamantanecarbonyl chloride (1eq) at 0°C and reaction mixture was then stirred at room temperature for 6 hours. Progress of reaction was checked using thin layer chromatography (TLC). Reaction mixture was extracted with dichloromethane and washed with water (30ml x 3). Organic layer was dried over sodium sulfate

and concentrated over high vacuum. Light green compound was obtained as product after hexane washings.

^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$) = 8.57 (d, J = 9.6 Hz, 1H), 7.58 – 7.51 (m, 5H), 7.48 – 7.42 (m, 2H), 7.39 – 7.34 (m, 1H), 7.25 (d, J = 8.2 Hz, 1H). 2.05 – 2.03 (m, 10H), 1.72 – 1.69 (m 5H). ^{13}C-NMR: δ/ppm (125 MHz, CDCl3) =175.8, 164.7, 157.2, 152.8, 137.2, 132.1, 131.08, 129.2, 128.4, 125.1, 124.7, 123.6, 123.4, 120.4, 119, 113.7, 113.3, 100.5, 41.3, 38.7, 36.3, 27.8. IR: υ max/cm-1 = 3020, 2955, 2228, 1724, 1634, 1584, 1533, 1501, 1391.2, 1343, 1273, 1229, 1151, 1030, 880, 754. HRMS: m/z calculated for $C_{31}H_{25}NO_4$: Exact Mass: 475.1784 , found $[MH]^+$ = 476. 1857; M.P. = 297°C; Yield = 69%.

Compound 2. To a tetrahydrofuran suspension of hydroxyl coumarin (1eq) was added triethylamine (2.5 eq) followed by the addition of 2-(bicyclo[2.2.1]heptan-2-yl)acetyl chloride (1.1eq) at 0°C and reaction mixture was then stirred at room temperature for 6 hours. Progress of reaction was checked using thin layer chromatography (TLC). Reaction mixture was extracted with ethyl acetate and washed with water (30ml x 3). Organic layer was dried over sodium sulfate and concentrated over high vacuum. Light green compound was obtained as product.

^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$) = 8.63 (d, J = 9.6 Hz, 1H), 7.65 – 7.60 (m, 5H), 7.53 – 7.51 (m, 2H), 7.46 – 7.44 (m, 1H), 7.32 (d, J = 8.9 Hz, 1H). 2.63 – 2.59 (m, 1H), 2.48 – 2.43 (m, 1 H), 2.30 (bs, 1H), 2.13 – 2.12 (m, 1H), 2.08 – 2.05 (m, 1H), 1.63 – 1.51 (m, 4H), 1.40 – 1.38 (m, 1H), 1.31 – 1.25 (m, 1H), 1.21 – 1.19 (m, 3H). ^{13}C-NMR: δ/ppm (125 MHz, $CDCl_3$) =171.1, 164.6, 157.1, 152.3, 137.2, 132.1, 131.0, 129.2, 128.4, 125.1, 124.8, 123.6, 123.3, 120.5, 118.9, 113.7, 113.3, 100.5, 41.26, 41.22, 38.4, 37.7, 36.7, 35.2, 29.7, 28.4. IR: υ max/cm^{-1} = 3120, 2950, 2234, 1730, 1620, 1581.5, 1542.6, 1511, 1391, 1349, 1273, 1229, 1166, 1020.8, 873, 746.

HRMS: m/z calculated for $C_{29}H_{23}NO_4$ Exact Mass: 449.1627, found $[MH]^+$ = 450.1699, $[M+Na]^+$ = 472.1521. M.P. = 210°C; Yield = 65%.

Synthesis of 2-(bicyclo[2.2.1]heptan-2-yl)acetyl chloride.

2-Norbornaneacetic acid (1eq) was dissolved in dry tetrahydrofuran and one drop of dimethylformamide was added. Thionyl chloride ($SOCl_2$, 2eq) was added dropwise at 0°C. Reaction mixture was then refluxed for 3 hours. Reaction mixture was then concentrated over vacuum to remove unreacted $SOCl_2$ and kept under nitrogen. The yellow liquid obtained was used immediately without any purification.

Table S1. Crystal data and structure refinement for compound **2**.

	Compound 2
Empirical formula	$C_{29}H_{23}NO_4$
Formula weight	449.48
Crystal System	Monoclinic
Space group	$P2_1/c$
a/Å	31.1736(9)
b/Å	9.5651(2)
c/Å	8.0016(3)
α,β, γ, deg	90, 91.296(3), 90.00
Volume/Å^3	2385.28(12)
Z, ρ_{calc}mg/mm^3, μ/mm^{-1}	4, 1.252, 0.673
Crystal size/mm^3	0.3017 × 0.087 × 0.0558
2Θ range for data collection	8.52 to 133.54°
Index ranges	$-36 \leq h \leq 37$, $-11 \leq k \leq 3$, $-9 \leq l \leq 9$
Reflections collected	7164
Independent reflections	4175[R(int) = 0.0187]
Data/restraints/parameters	4175/0/307
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1911
Final R indexes [all data]	R_1 = 0.0783, wR_2 = 0.2066
Largest diff. peak/hole / e Å^{-3}	0.39/-0.26

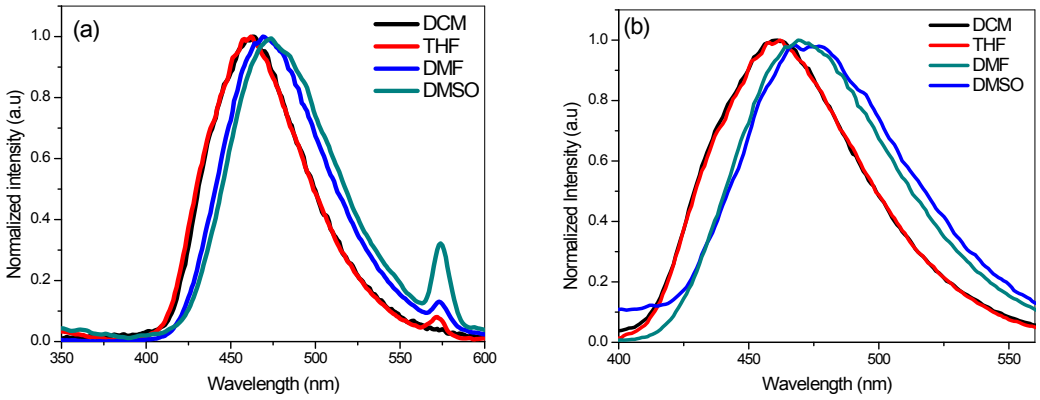


Fig. S1 Photoluminescence solvatochromism spectra for (a) compound **1** and (b) **2**.

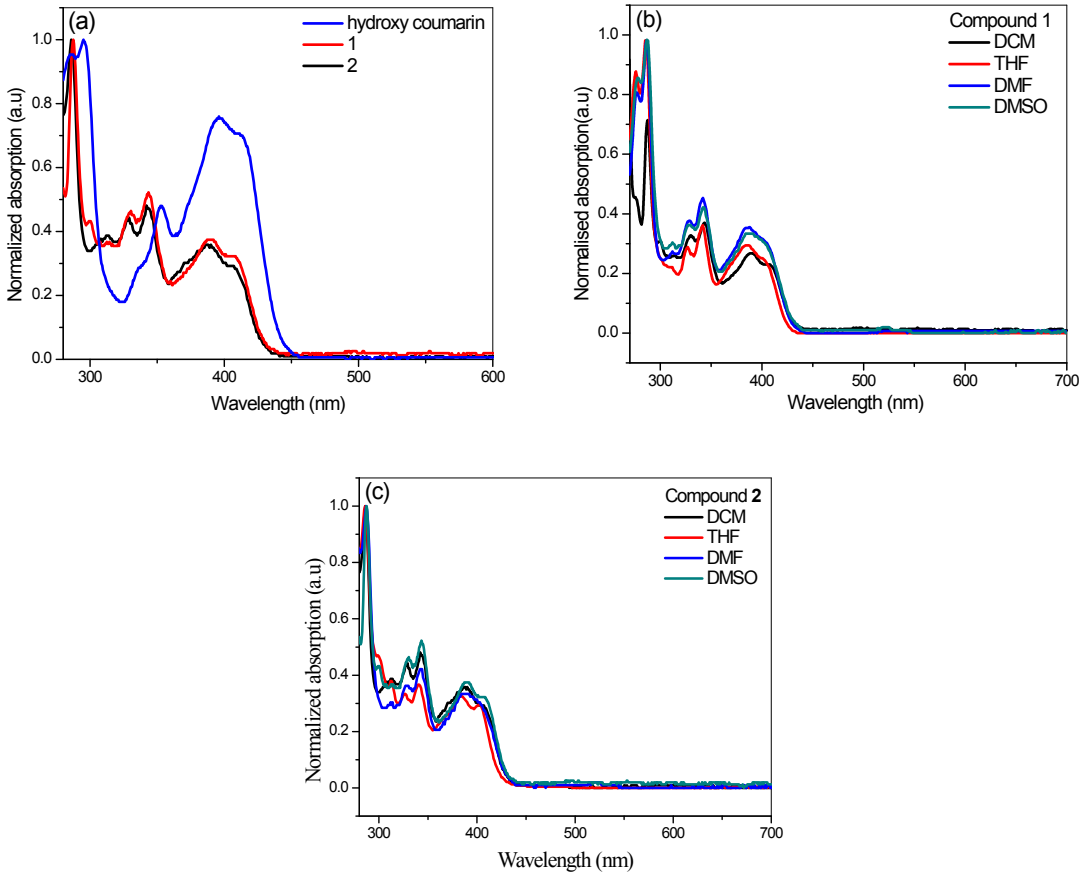


Fig. S2 (a) Comparison of UV-vis absorption spectra of **1** and **2** with parent hydroxyl coumarin; (b) UV-vis absorption solvatochromism spectra for **1** and (c) UV-vis absorption solvatochromism spectra for **2**.

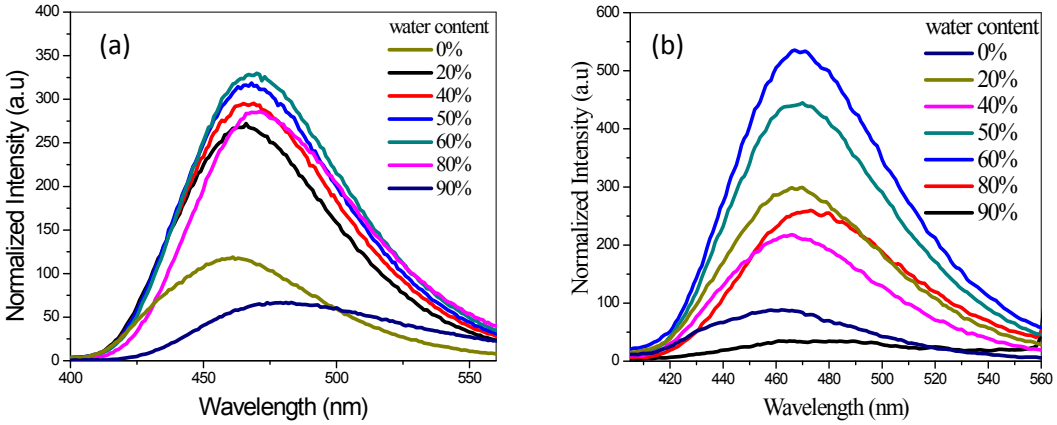


Fig. S3. PL changes in THF:water experiment with increasing water content for compounds **1** (a) and **2** (b).

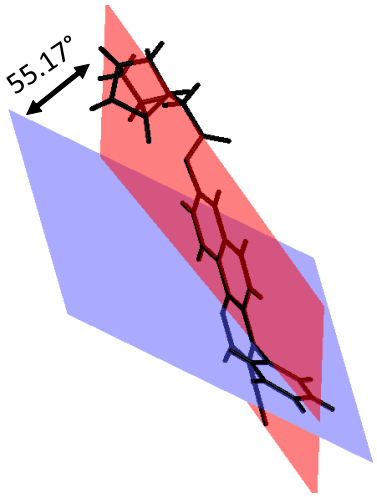


Fig. S4 Interplanar angle between 2H-benzo[h]chromen-2-one core and phenyl moiety of compound **2**.

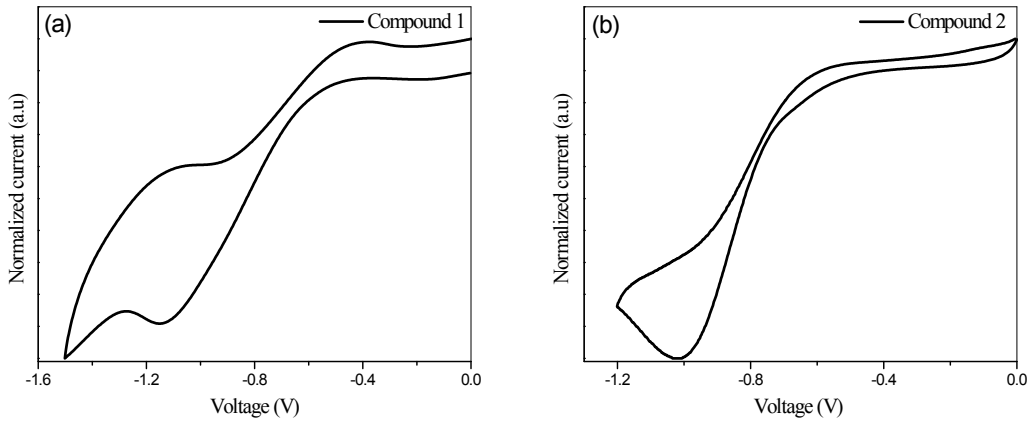


Fig. S5 Cyclic voltammetry curves showing reduction potential window for compound **1** and **2**. (E_{LUMO} = -[(E_{red} + 4.8)] eV, where E_{red} is the onset reduction potential relative to the (Fc/Fc^{+}) couple. $E_{1/2}$ (Fc/Fc^{+}) = 0.58 eV (DCM) and 0.55 (ACN). E_{HOMO} = E_{LUMO} + E_g).

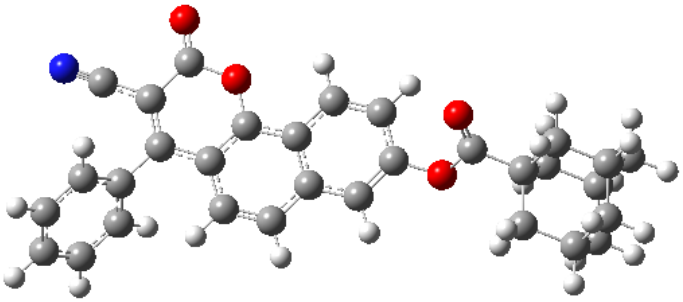


Fig. S6 Optimized geometry of compound **1** calculated at B3LYP/6-311G (d,p) level of DFT.

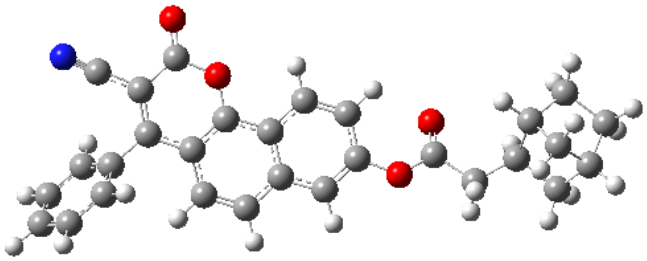


Fig. S7 Optimized geometry of compound **2** calculated at B3LYP/6-311G (d,p) level of DFT.

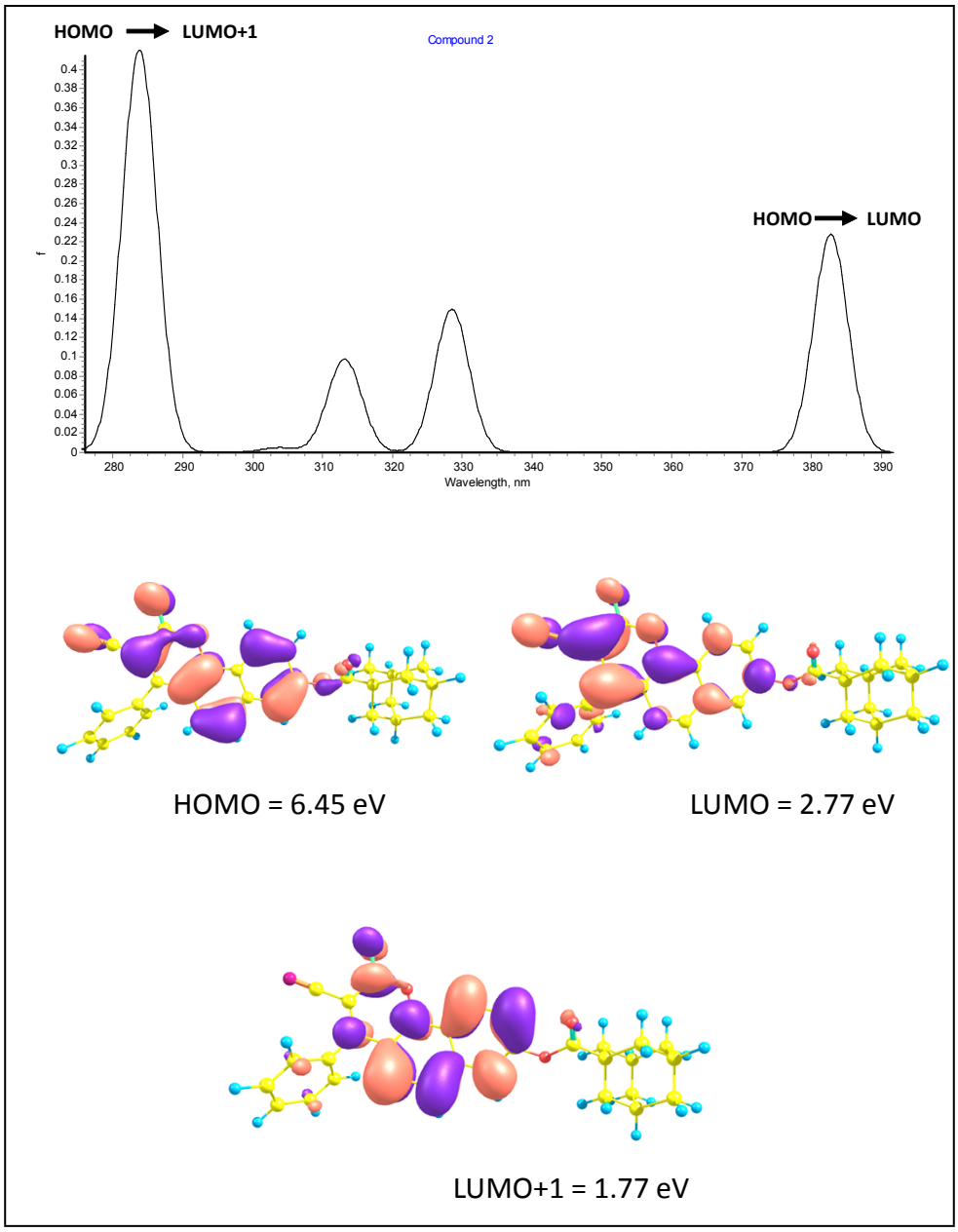


Fig. S8 TD-DFT absorption spectra of compound **1** calculated atB3LYP/6-311G(d,p) level. Peaks are characterized with their major electronic transition. Orbitals involved in electronic transitions are also depicted.

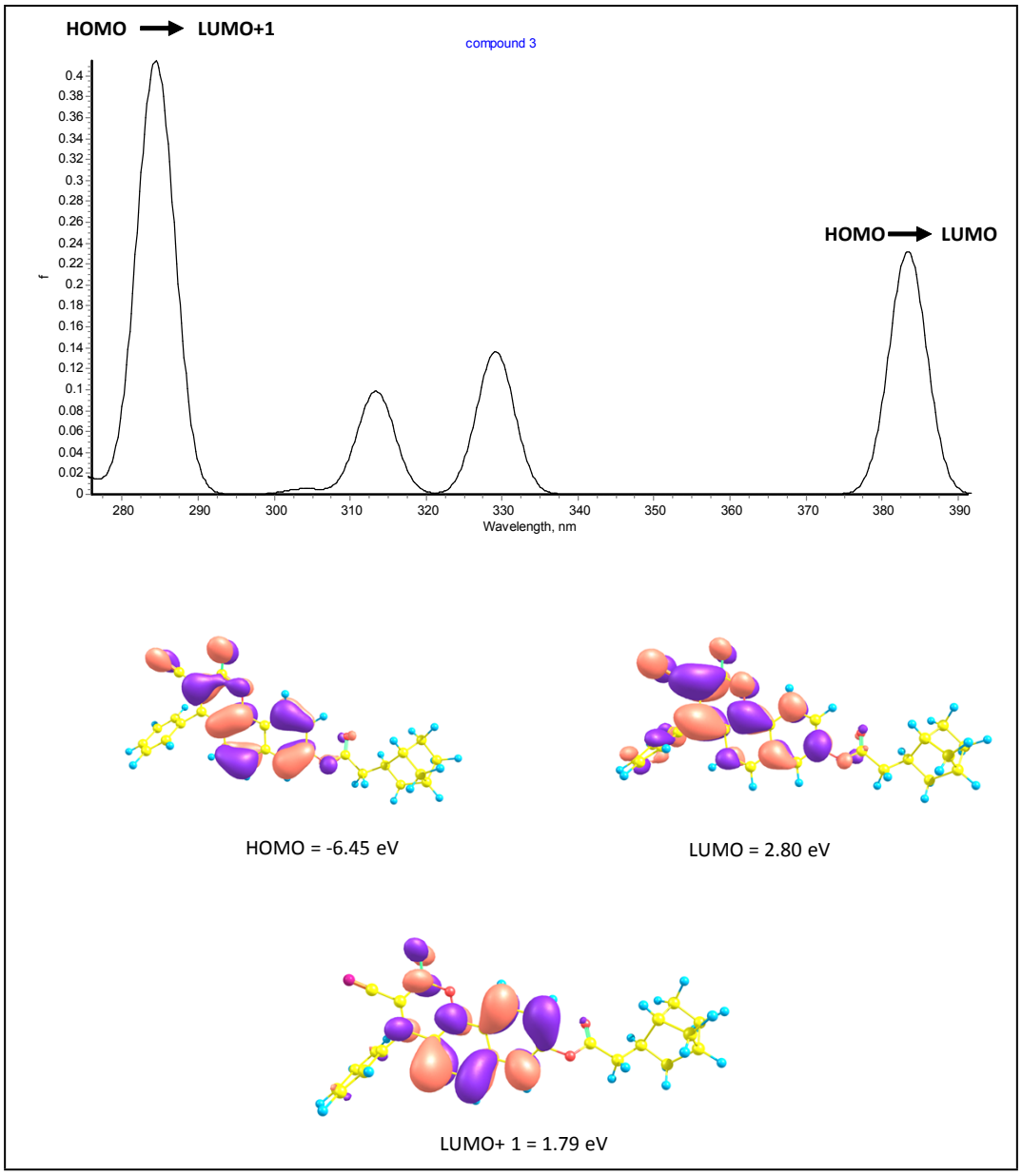


Fig. S9 TD-DFT absorption spectra of compound **2** calculated atB3LYP/6-311G(d,p) level. Peaks are characterized with their major electronic transition. Orbitals involved in electronic transitions are also depicted.

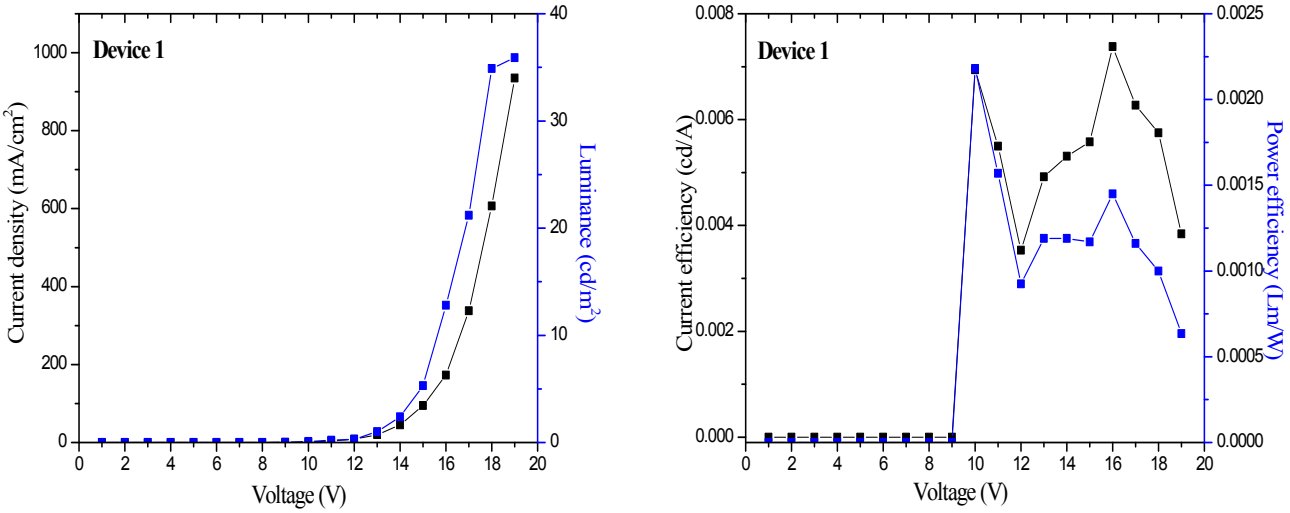


Fig. S10 J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 1.

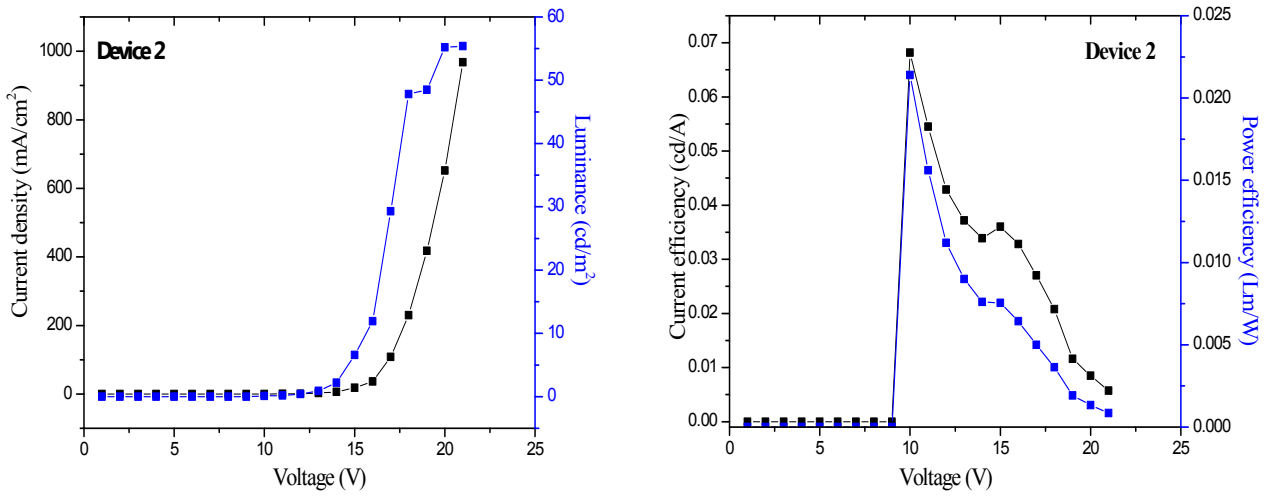


Fig. S11 J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 2.

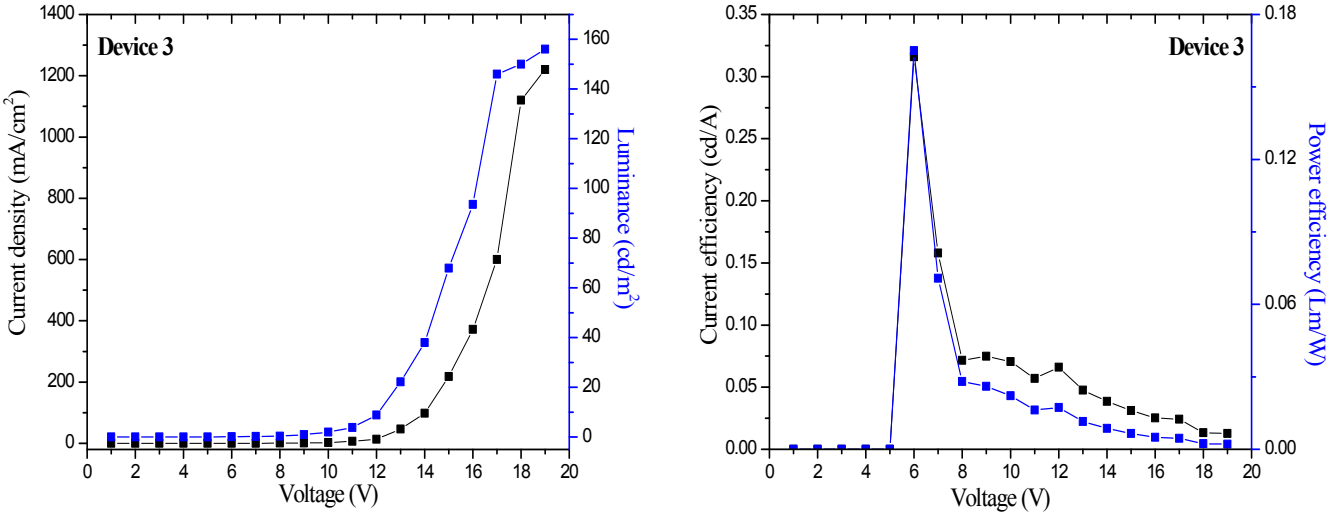


Fig. S12 J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 3.

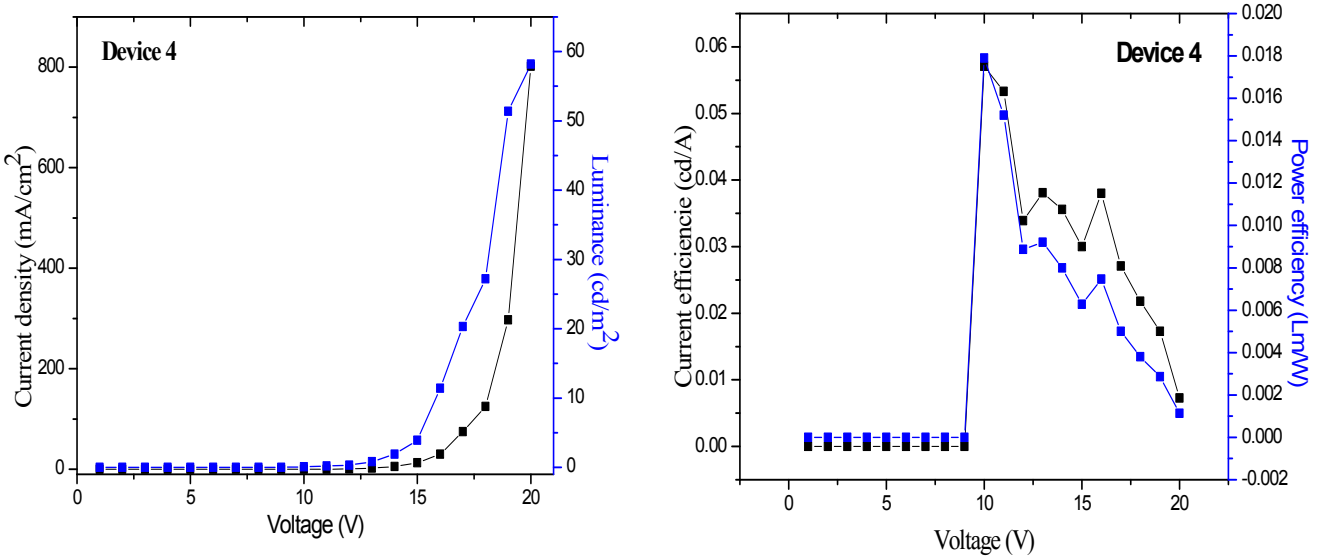


Fig. S13 J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 4.

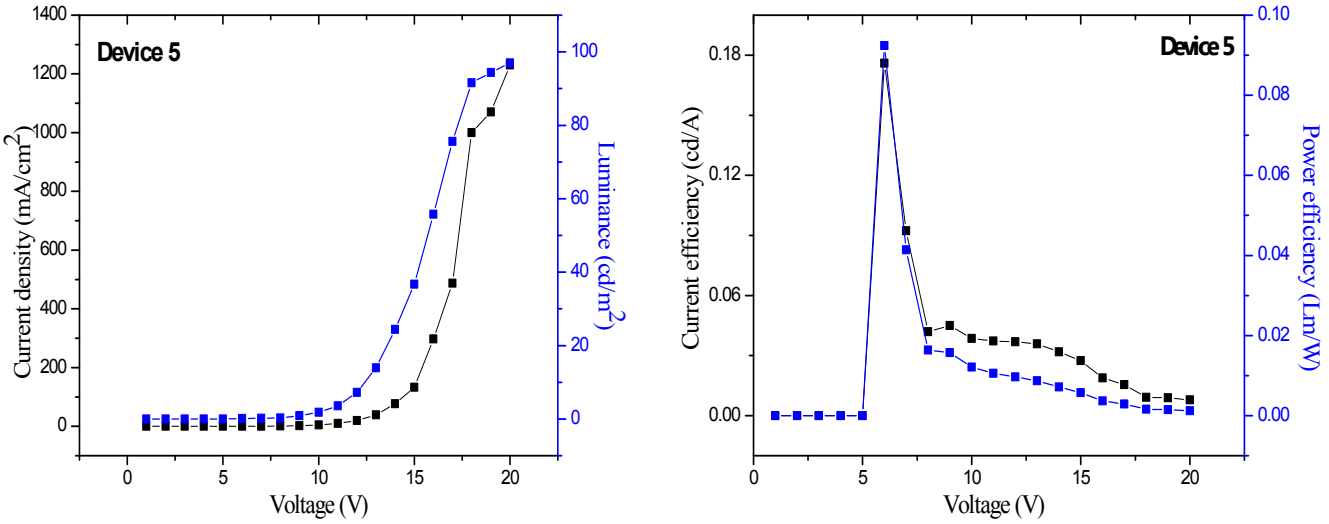


Fig. S14 J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 5.

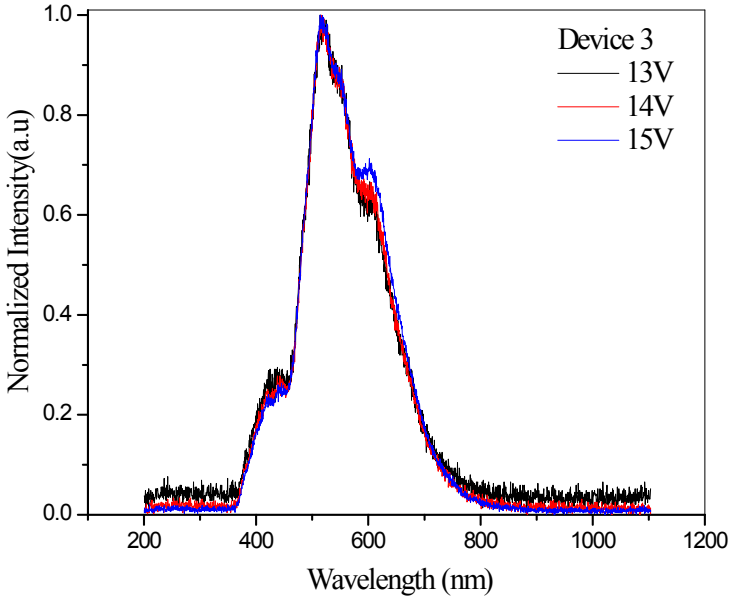


Fig. S15 Electroluminescence spectrum of Device 3 at 13V, 14V and 15V.

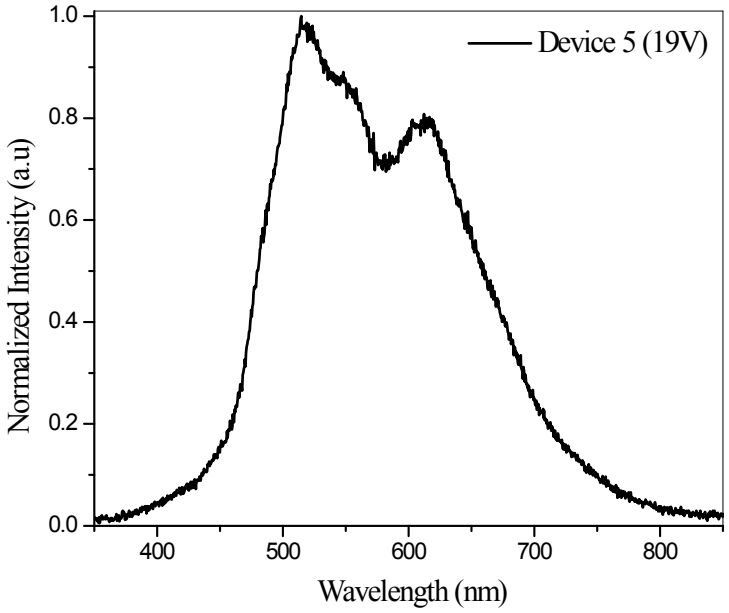


Fig. S16 Electroluminescence spectrum of Device 5 at 19V.

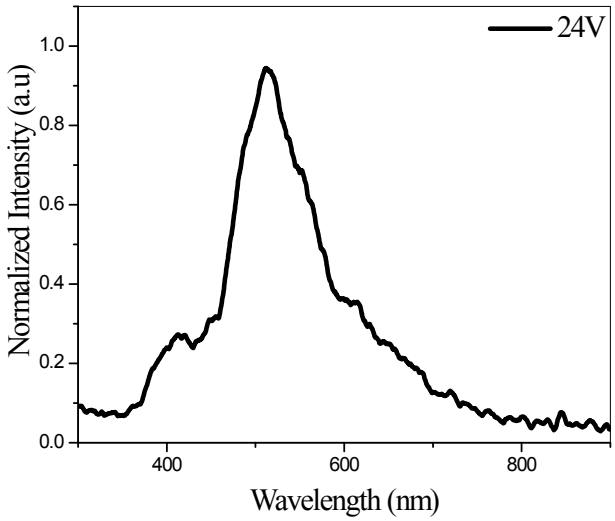


Fig. S17 Electroluminescence spectrum of Device 6 at 24V.

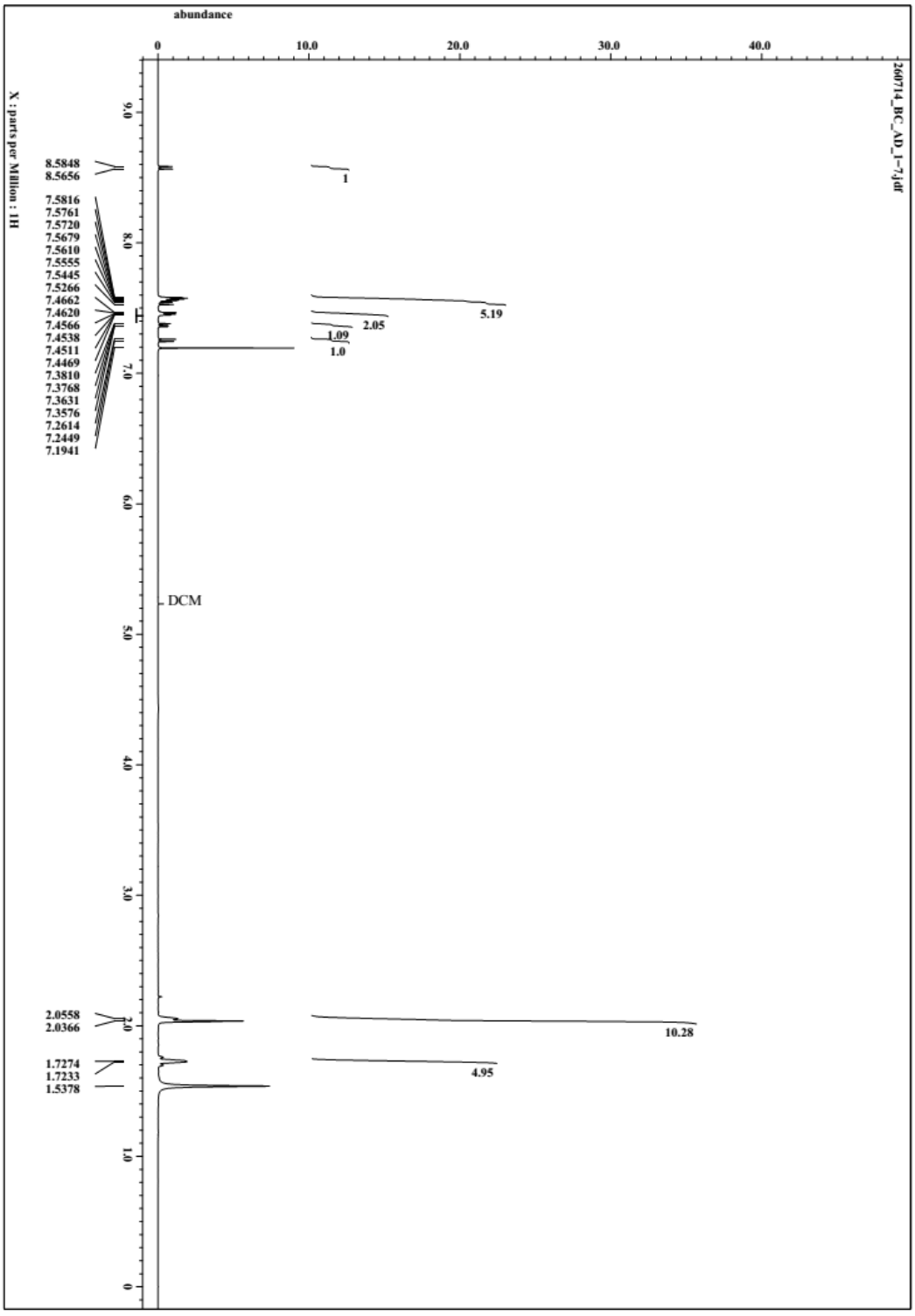


Fig. S18 ^{1}H-NMR spectrum of compound **1**.

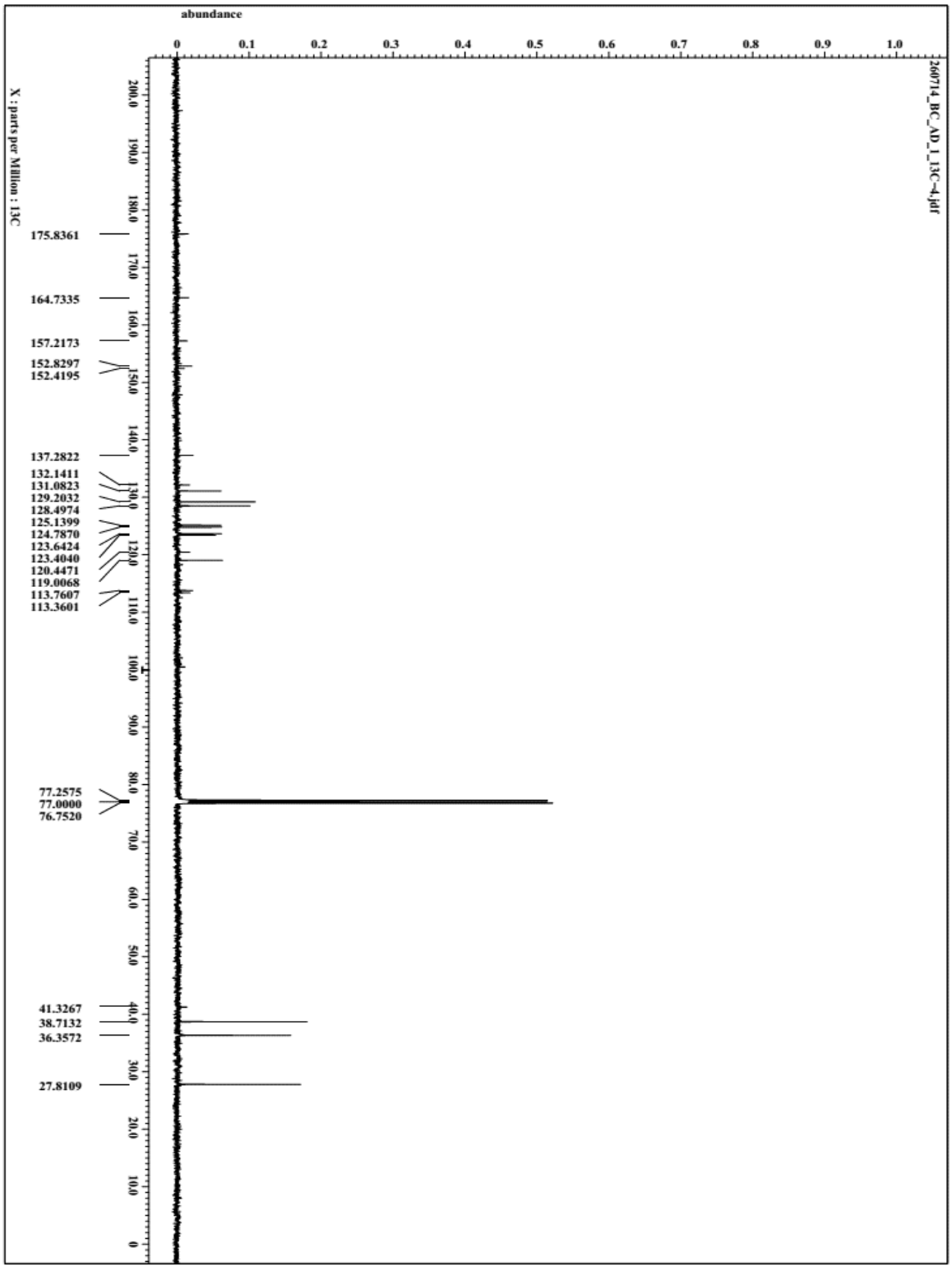


Fig. S19 ^{13}C-NMR spectrum of compound **1**.

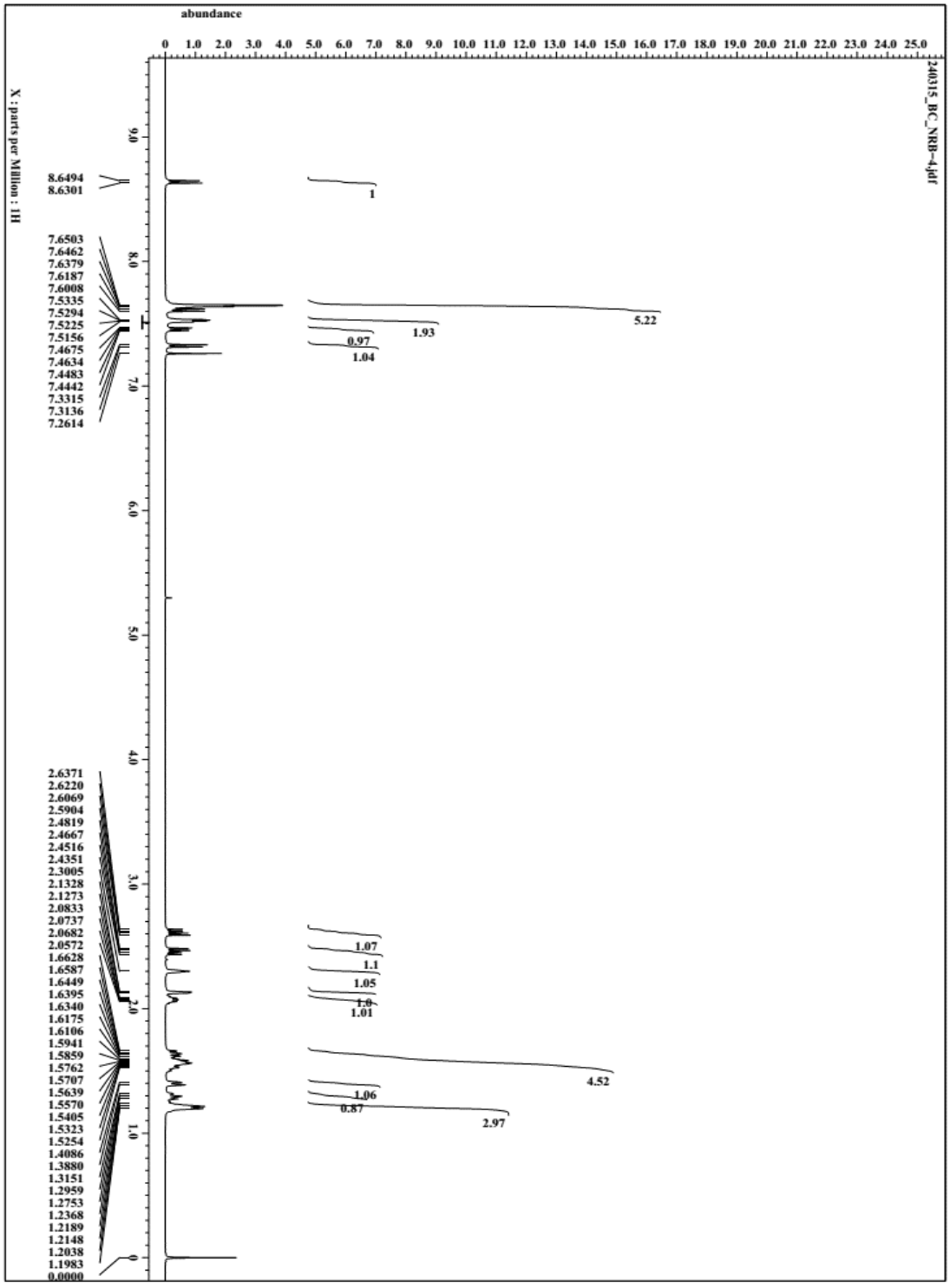


Fig. S20 ^{1}H-NMR spectrum of Compound **2**.

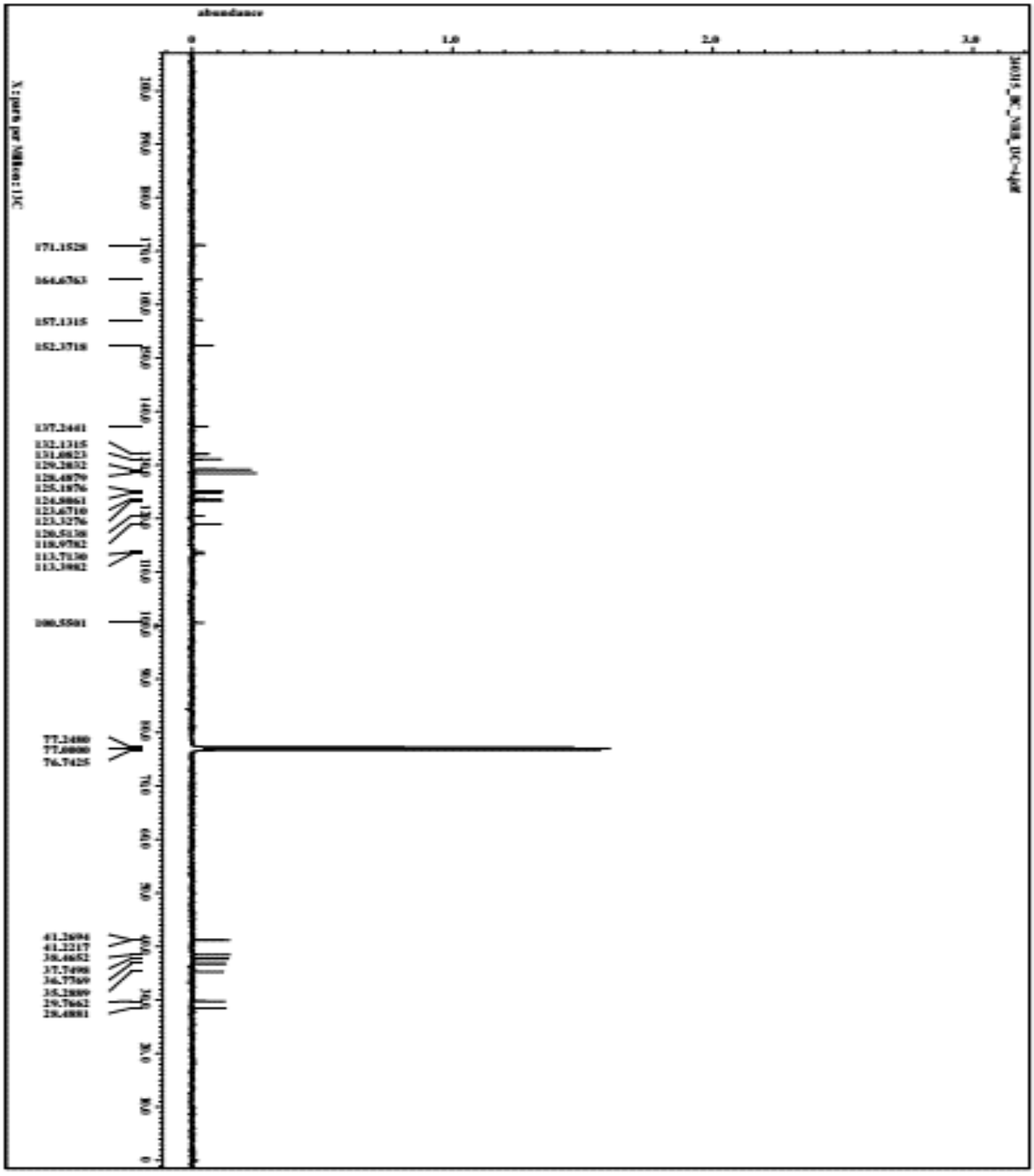


Fig. S21 ^{13}C-NMR spectrum of Compound **2**.