Supporting Information

Molecular Cocrystals with Hydrogen-Bonded Polymeric Structures and Polarized Luminescence

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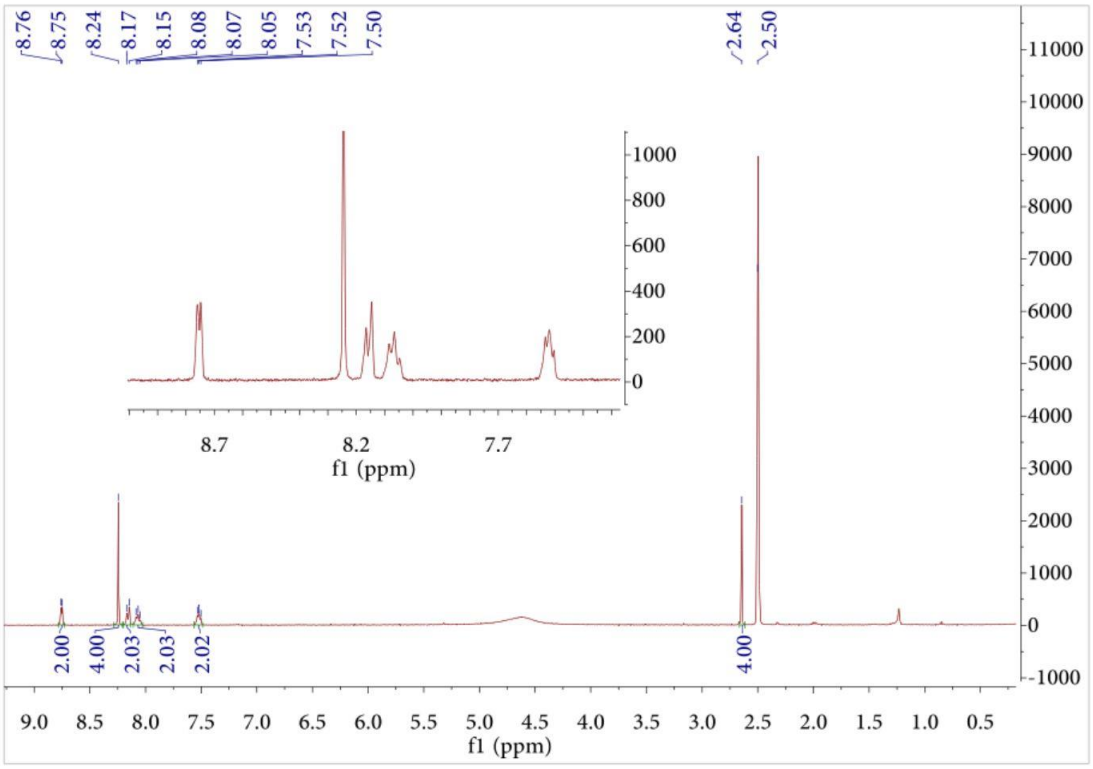

Figure S1. ^{1}H NMR spectrum of **4** in DMSO-d$_6$.

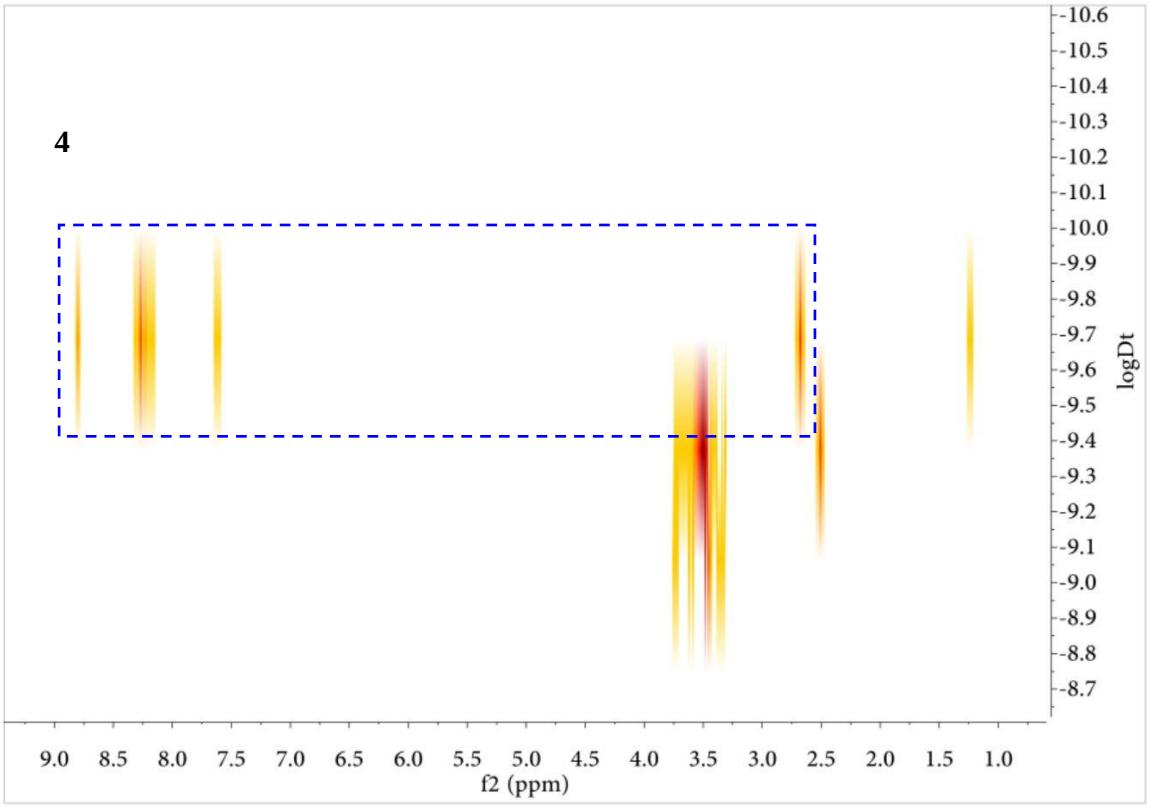

Figure S2. ^{1}H DOSY NMR spectrum of **4** in DMSO-d$_6$.

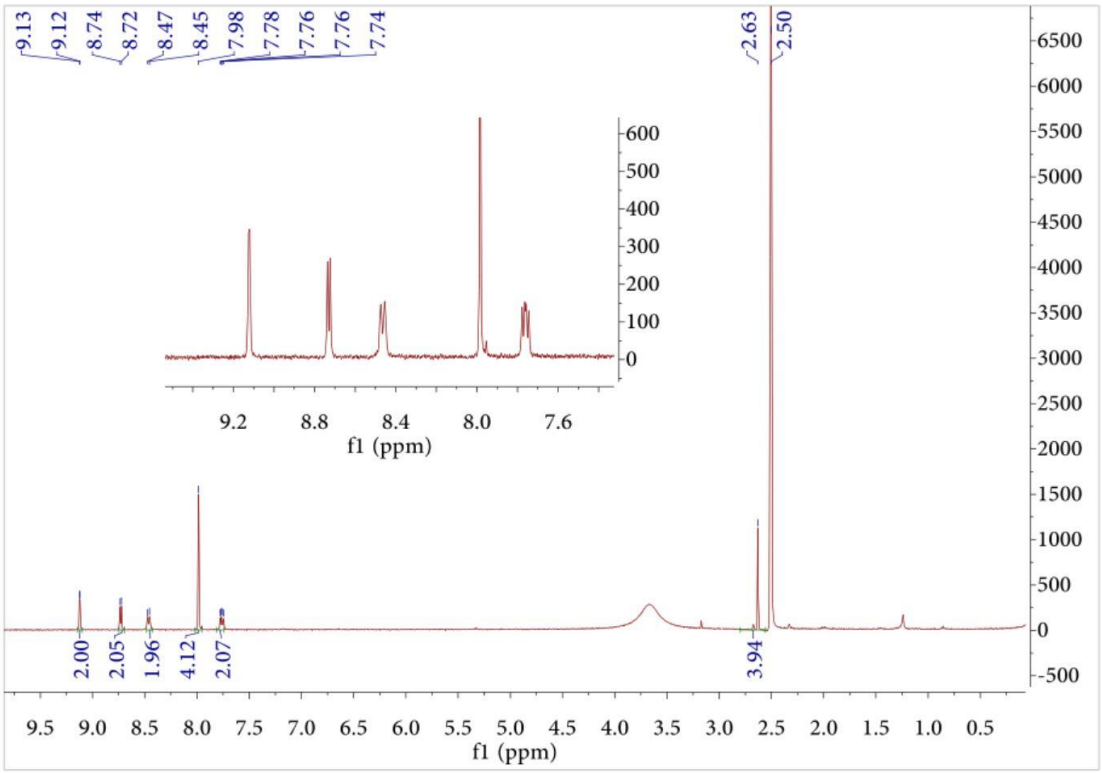

Figure S3. ^{1}H NMR spectrum of **5** in DMSO-d$_6$.

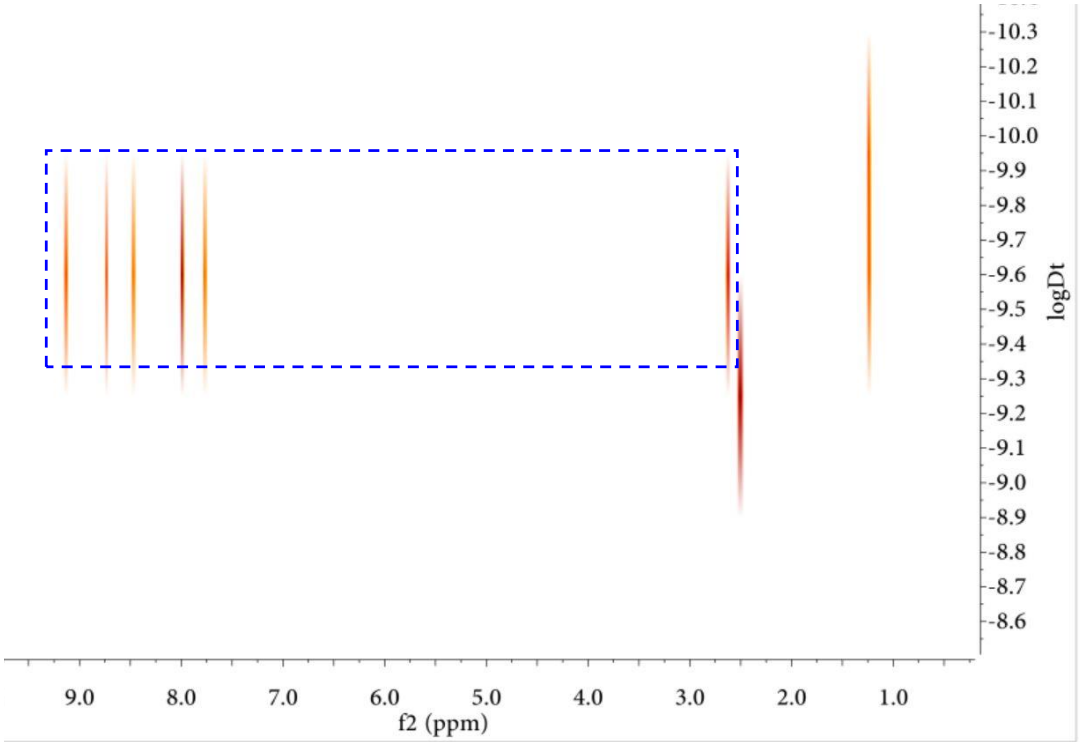

Figure S4. ^{1}H DOSY NMR spectrum of **5** in DMSO-d$_6$.

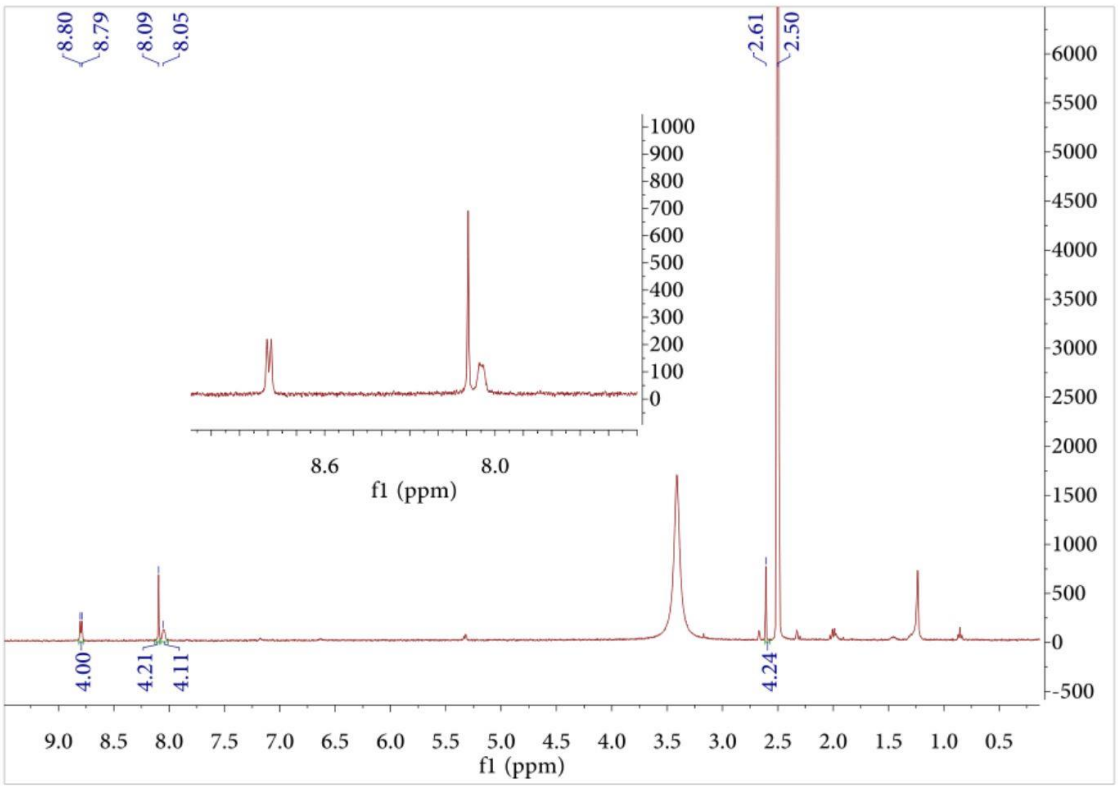

Figure S5. ^{1}H NMR spectrum of **6** in DMSO-d$_6$.

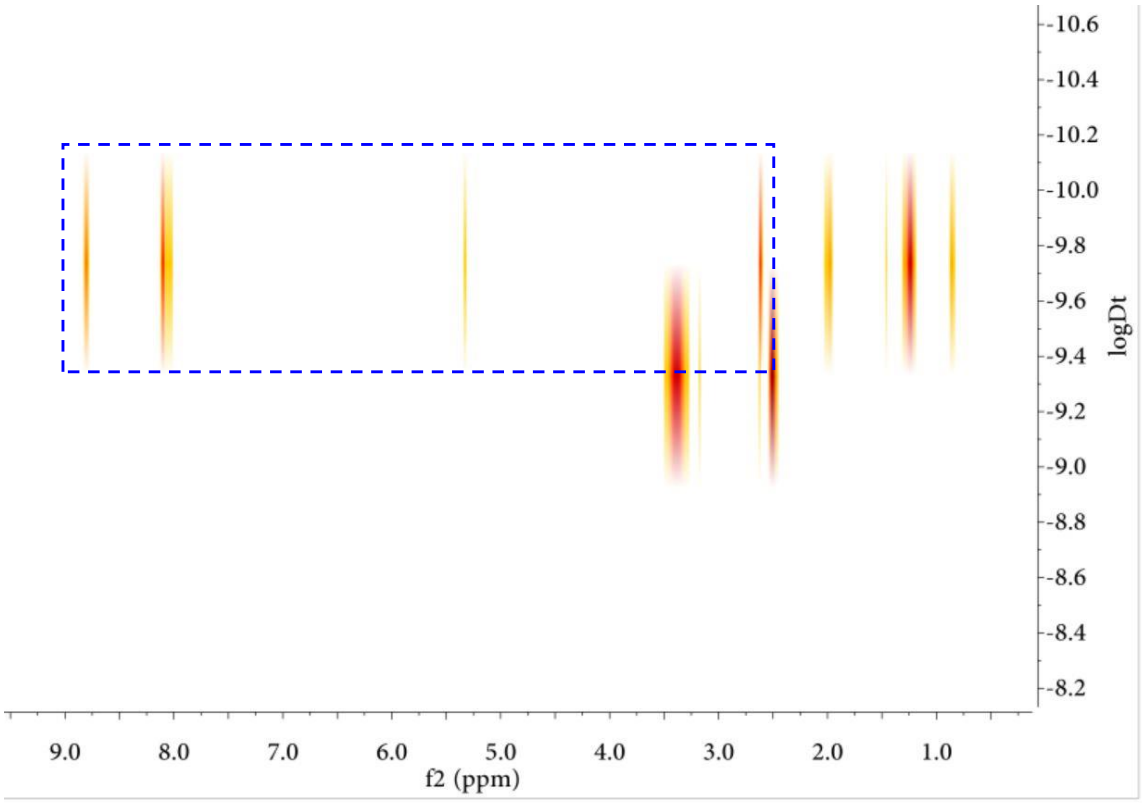

Figure S6. ^{1}H DOSY NMR spectrum of **6** in DMSO-d$_6$.

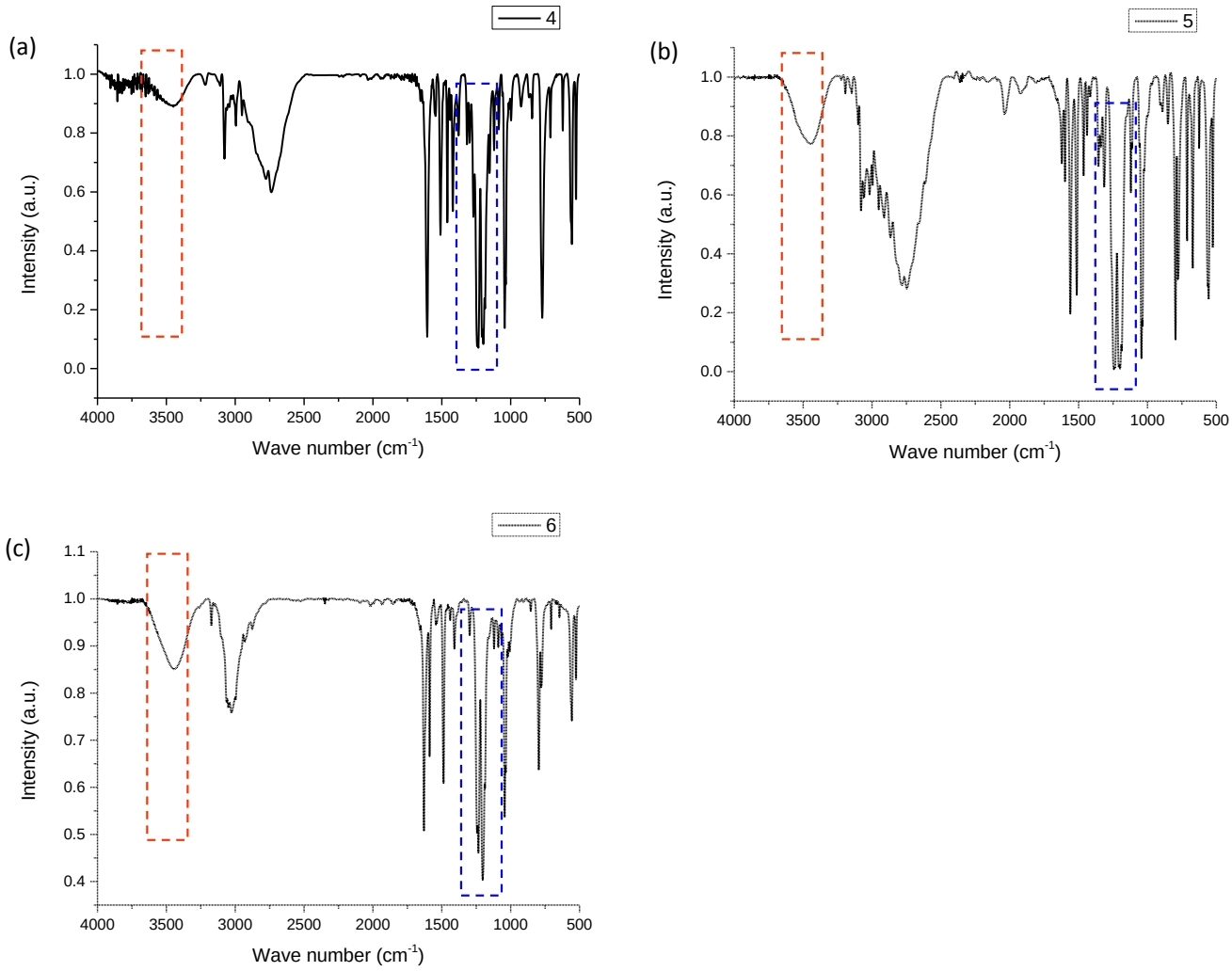

Figure S7. FTIR spectrum of the microcrystals of (a) **4**, (b) **5**, and (c) **6** as KBr pellet. The bands at around 3500 cm^{-1} are assigned to the vibrations of hydrogen bonds. The two bands at around 1200 cm^{-1} are ascribed to the symmetric and asymmetric stretching vibrations of the sulfonate groups.

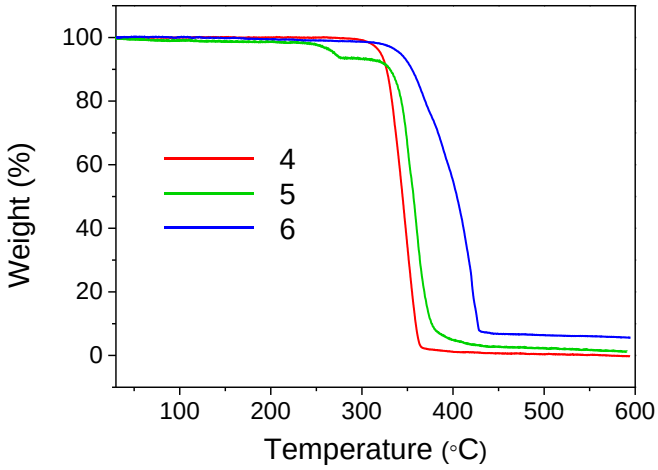

Figure S8. Thermogravimetric analysis (TGA) of the microcrystals of **4**, **5**, and **6** with a temperature rate of 10 °C /min in a nitrogen environment (200 mL/min).

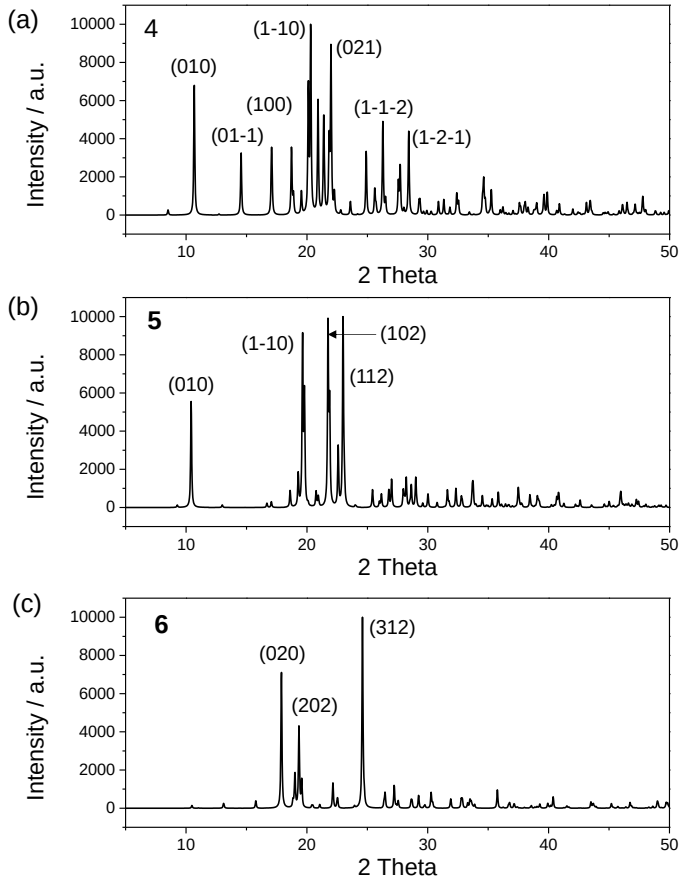

Figure S9. Simulated powder XRD patterns of (a) **4**, (b) **5**, and (c) **6** based on their single-crystal data.

Table S1. Photophysics data of microcrystals of **4** – **6**.[a]

Compound	λ_{emi}/nm	Φ/%	τ/ns	$k_r/10^7$ s^{-1}	$k_{nr}/10^7$ s^{-1}
4	385	12.9	4.8	2.67	18.03
5	456	27.7	11.7	2.38	6.20
6	466	18.0	1.8	9.94	45.30

[a] Φ is absolute quantum yield. τ is averaged life time. See further details in Figure S2. $k_r = \Phi/\tau$; $k_{nr} = (1 - \Phi)/\tau$.

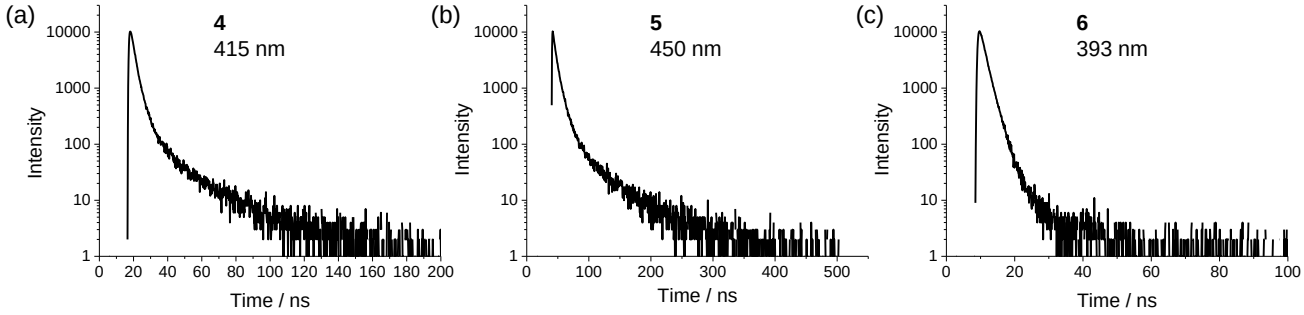

Figure S10. Lifetime decay curves for microcrystals of (a) **4**, (b) **5**, and (c) **6**.

Decay curves for microcrystals of **4**, and **5** are tri-exponentially fitted and the decay of **6** is bi-exponentially fitted. The average lifetimes (τ_{ave}) are reported in Table S1, which are determined by $\tau_{ave} = \alpha_1\tau_1 + \alpha_2\tau_2 + \alpha_3\tau_3$.

For microcrystals of **4**, τ_{ave} = 4.83 ns, τ_1 = 2.27 ns, τ_2 = 6.56 ns, τ_3 = 24.11 ns, α_1 = 74.9%, α_2 = 16.7%, α_3 = 8.4%;

for microcrystals of **5**, τ_{ave} = 11.66 ns, τ_1 = 3.72 ns, τ_2 = 8.70 ns, τ_3 = 42.34 ns, α_1 = 32.0%, α_2 = 54.4%, α_3 = 13.6%;

for microcrystals of **6**, τ_{ave} = 1.81 ns, τ_1 = 1.53 ns, τ_2 = 3.47 ns, α_1 = 85.8%, α_2 = 14.2%.

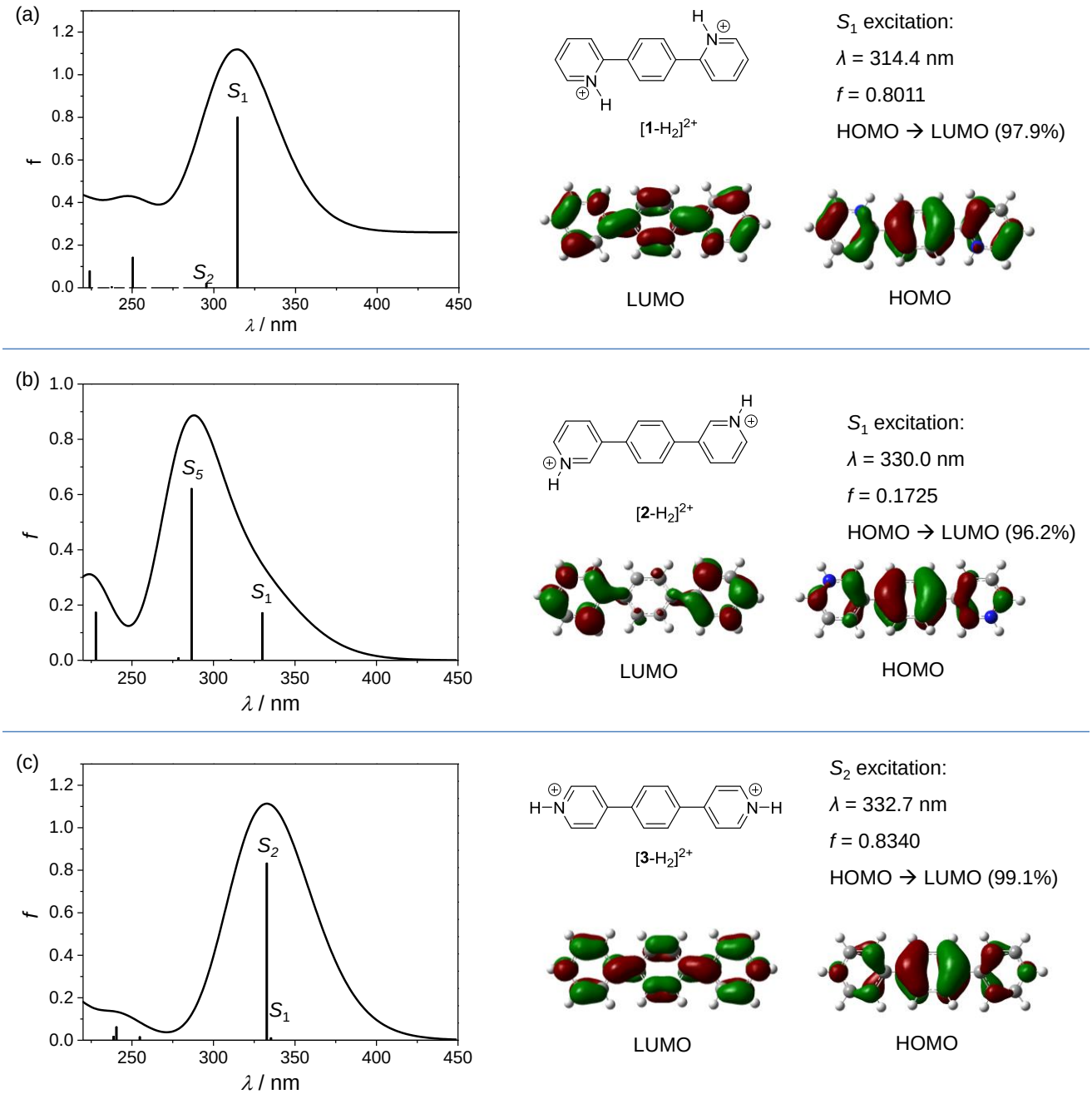

Figure S11. TDDFT calculation results of (a) [**1**-H_2]$^{2+}$, (b) [**2**-H_2]$^{2+}$, and (c) [**3**-H_2]$^{2+}$. Left: TDDFT-predicted vertical excitations. Right: chemical structures, DFT-calculated frontier orbitals, and the calculated wavelength (λ), oscillator strength (f), and percent contribution for the HOMO→LUMO excitation.

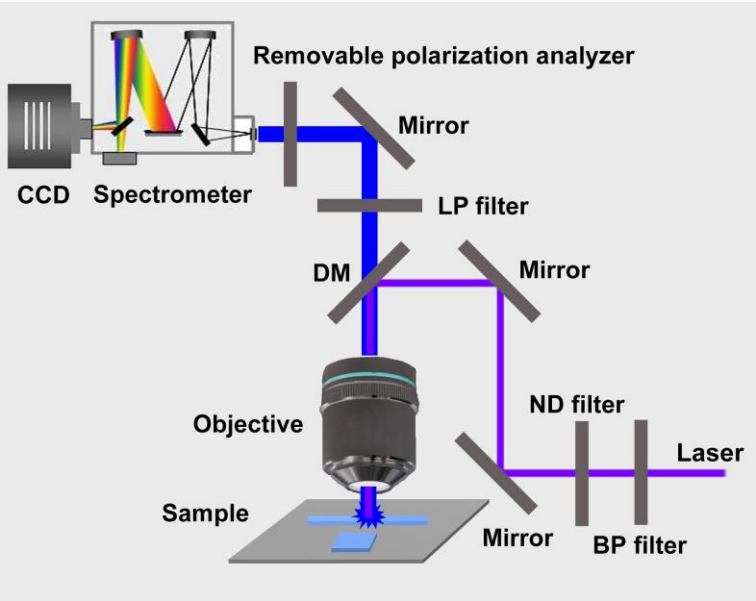

Figure S12. Schematic demonstration of the experimental setup for polarized luminescence characterization for a single microcrystal. CCD: charge coupled device; LP filter: long-pass filter; DM: dichromic mirror; ND filter: neutral density filter; BP filter: band-pass filter. The polarization luminescence information of the microcrystal is probed by a removable polarization analyzer plate.

The excitation laser beam (CW, 405 nm) was filtered with a 405/10 nm band-pass filter and then focused down to a 10-μm diameter spot through an objective lens (Olympus M Plan, × 20, N.A. = 0.4) as a nearly uniform pump source. The power at the input was altered by a neutral density filter. The emissions from individual microcrystals were collected by the same objective with a back-scattering configuration and analyzed by Prinston Instrument HRS-300S spectrometer with a thermoelectric-cooled PIXIS 256BR CCD after removing the excitation beam with a 420-nm long-pass filter. The removable polarization analyzer was used before the spectrometer when collecting polarized luminescent spectra of the microcrystals.