

Electronic Supporting Information (ESI) for

Aggregation-induced ratiometric emission and mechanochromic luminescence in pyrene-benzohydrazone conjugate

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General remarks

¹H NMR spectra were obtained from a solution in deuterated DMSO using a Bruker-400 spectrometer (s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet). Elemental analyses (C, H, and N) were conducted with a Perkin-Elmer 2400 analyzer. Solid-state UV-vis spectra were recorded on a SHIMADZU UV-3600 UV-vis-NIR spectrophotometer. Powder X-ray diffraction (PXRD) was recorded on a RINT 2000 vertical goniometer with Cu K α X-ray source (operated at 40 kV and 100 mA). Steady PL and photoluminescence excitation (PLE) spectra were recorded by an Edinburgh FS5 steady state fluorescence spectrophotometer equipped with a 450 W xenon lamp. The absolute emission quantum yields were measured using a Quantum Yield Measurement System from Edinburgh FS5 coupled with an integrating sphere as the sample chamber and a multichannel analyzer for signal detection.

Materials and reagents

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The model complex **ph-ph** was synthesized and characterized according to the literature method.¹ The single crystals suitable for X-ray diffraction were obtained by standing MeOH solution of ph-ph after several days in the dark. IR (solid KBr pellet) 1638(s), 1552(m), 1400(s), 1287(m), 1142(m), 970(w), 912(w) and 693(m) cm⁻¹.

Synthesis of pyrenyl-containing carbohydrozone derivatives

General procedure for the synthesis of pyrenyl-containing carbohydrozone derivatives. A round flask with a magnetic stir bar was charged with pyrene-1-carbaldehyde (230.2 mg, 1.0 mmol), benzoyl hydrazine derivatives (1.0 mmol) and several drops of glacial acetic acid in methanol (10 mL). After stirring at 80 °C for 3 h, the crude product was obtained by filtration. The residue was recrystallized from DMF and was dried in vacuum to get the target compound.

Benzoic acid pyren-1-ylmethylene-hydrazide (1). Following the general procedure, benzoic acid hydrazide (136.1 mg, 1.0 mmol) was used. Yield: 87% ¹H NMR (400 MHz, DMSO) δ 12.07 (s, 1H), 9.54 (s, 1H), 8.84 (d, J = 9.4 Hz, 1H), 8.60 (d, J = 8.1 Hz, 1H), 8.39 (d, J = 7.6 Hz, 4H), 8.27 (q, J = 8.9 Hz, 2H), 8.14 (t, J = 7.6 Hz, 1H), 8.02 (d, J = 7.1 Hz, 2H), 7.71 – 7.52 (m, 3H). Anal. Calcd for C₂₄H₁₆N₂O: H, 4.63; C, 82.74; N, 8.04. Found: H, 5.02; C, 83.19; N, 8.14.

4-Chloro-benzoic acid pyren-1-ylmethylene-hydrazide (2). Following the general procedure, 4-chloro-benzoic acid hydrazide (170.6 mg, 1.0 mmol) was used. Yield: 84% ¹H NMR (400 MHz,

DMSO) δ 12.13 (s, 1H), 9.52 (s, 1H), 8.84 (d, $J = 9.4$ Hz, 1H), 8.59 (d, $J = 8.1$ Hz, 1H), 8.47 – 8.34 (m, 4H), 8.27 (dd, $J = 18.8, 8.9$ Hz, 3H), 8.15 (t, $J = 7.6$ Hz, 1H), 8.04 (d, $J = 8.5$ Hz, 2H), 7.69 (d, $J = 8.5$ Hz, 2H). Anal. Calcd for $C_{24}H_{15}N_2ClO$: H, 3.95; C, 75.29; N, 7.32. Found: H, 4.01; C, 75.18; N, 7.44.

4-Methoxy-benzoic acid pyren-1-ylmethylene-hydrazide (3). Following the general procedure, 4-methoxy-benzoic acid hydrazide (166.1 mg, 1.0 mmol) was used. Yield: 86% 1H NMR (400 MHz, DMSO) δ 11.95 (s, 1H), 9.52 (s, 1H), 8.83 (d, $J = 9.2$ Hz, 1H), 8.59 (d, $J = 8.1$ Hz, 1H), 8.39 (d, $J = 7.7$ Hz, 1H), 8.27 (q, $J = 8.9$ Hz, 1H), 8.14 (t, $J = 7.6$ Hz, 1H), 8.01 (d, $J = 8.8$ Hz, 1H), 7.13 (d, $J = 8.8$ Hz, 1H), 3.87 (s, 1H). Anal. Calcd for $C_{25}H_{18}N_2O$: H, 5.00; C, 82.85; N, 7.73. Found: H, 5.15; C, 83.17; N, 7.45.

Crystal Structure Determination The diffraction intensity data was collected on a Bruker APEX-2 CCD with graphite-monochromated Cu-K α radiation ($\lambda = 1.54178\text{\AA}$). Data collection, data reduction and cell refinement were performed by using the Bruker Instrument Service v4.2.2 and SAINT V8.34A software.^{2,3} Structures were solved by direct methods using the SHELXS program, and refinement was performed using SHELXL based on F^2 through full-matrix least squares routine.⁴ Absorption corrections were applied upon using multi-scan program SADABS.⁵ Hydrogen atoms of organic ligands were generated geometrically by the riding mode and all the non-hydrogen atoms were refined anisotropically through full-matrix least-squares technique on F^2 with the SHELXTL program package.^{6,7} A summary of the crystallographic data and refinement parameters is shown in Table S1.

Table S1. Crystallographic data and structure refinement for complex **ph-ph**.

| Complex | ph-ph |
|---|--|
| Formula | C ₁₄ H ₁₂ N ₂ O |
| <i>Mr</i> [g mol ⁻¹] | 224.26 |
| Crystal system | orthorhombic |
| Space group | <i>Pna</i> 21 |
| Crystal colour | white |
| Crystal description | needle |
| <i>a</i> [Å] | 8.7913(7) |
| <i>b</i> [Å] | 10.4651(8) |
| <i>c</i> [Å] | 13.1287(11) |
| α [°] | 90 |
| β [°] | 90 |
| γ [°] | 90 |
| <i>V</i> [Å ³] | 1207.86(17) |
| <i>Z</i> | 4 |
| ρ_{calcd} [g cm ⁻³] | 1.233 |
| μ (Mo-K α) [mm ⁻¹] | 0.634 |
| <i>F</i> (000) | 472 |
| θ range [°] | 1.696/24.998 |
| $R_1^a/wR_2^b(I > 2\sigma(I))$ | 0.0388/0.0984 |
| $R_1/wR_2(\text{all data})$ | 0.0435/0.1027 |
| GOF ^c on F^2 | 1.028 |

$$^a R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

$$^c \text{Goodness-of-fit} = [\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{params}})]^{1/2}, \text{ based on the data } I > 2\sigma(I).$$

Table S2. Photophysical properties of compounds **1** to **3**.

| Groups | $\lambda^{\text{abs}}_{\text{max}}/\text{nm}$ | $\lambda^{\text{ex}}/\text{nm}$ | $\lambda^{\text{em}}_{\text{max}}/\text{nm}$ | | | | Q.Y/% | | | |
|------------------|---|---------------------------------|--|----------|-------|--------|--------------|------|-------|--------|
| | | | sol | agg | solid | ground | sol | agg | solid | ground |
| H (1) | 370 | 365 | 413 | 446, 504 | 502 | 520 | 8.51 | 21.8 | 54.5 | 29.8 |
| Cl (2) | 371 | 365 | 416 | 440, 547 | 468 | 532 | 17.1 | 36.2 | 4.81 | 7.16 |
| OMe (3) | 371 | 365 | 412 | 444, 532 | 452 | 526 | 15.6 | 23.7 | 3.79 | 7.73 |

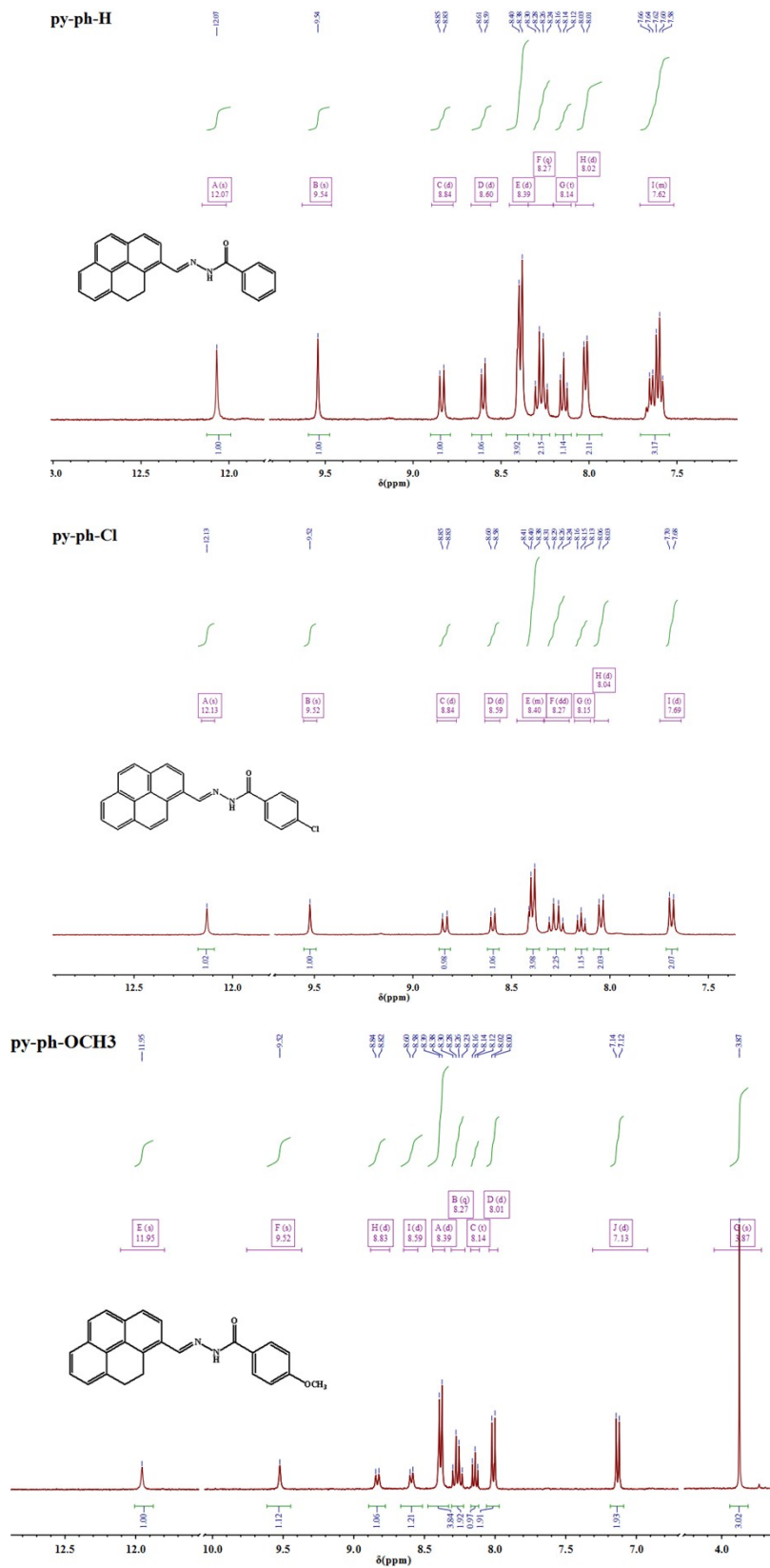


Figure S1. ^1H NMR spectra of **1-3** in $\text{DMSO-}d_6$.

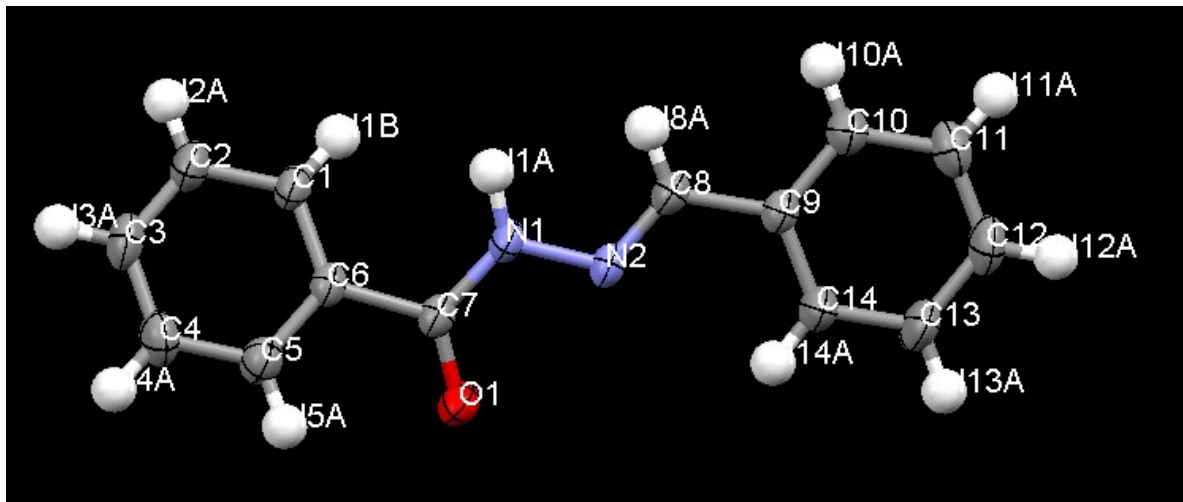


Figure S2. The ORTEP diagram of crystal structure, **ph-ph**.

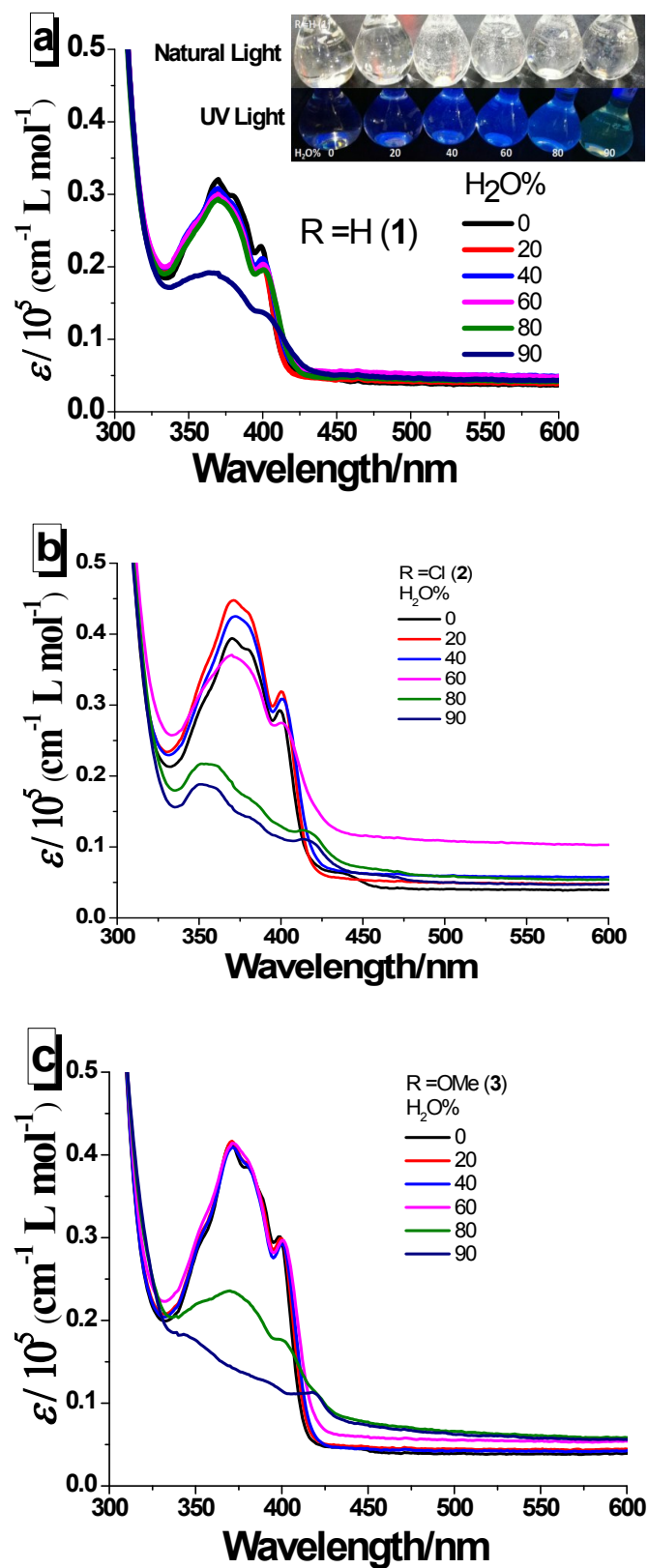


Figure S3. UV-vis spectras of pyrenyl-containing carbohydrozone derivatives **1-3** (10^{-5} mol/L) in aqueous DMF with the different water fraction.

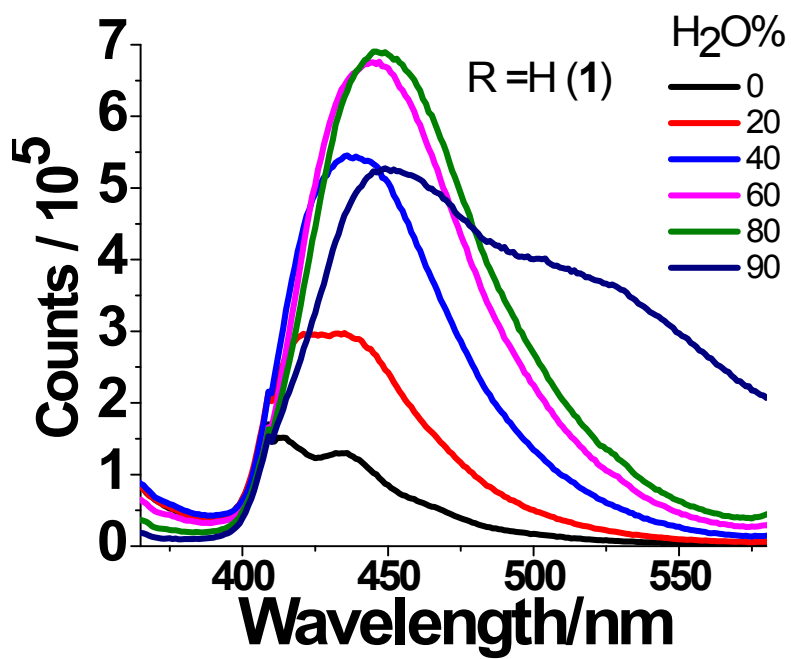


Figure S4. PL spectra of pyrenyl-containing carbohydrozone derivative **1** in DMF/H₂O mixtures with different volume fractions of H₂O. For the compound **2** and **3**, see main text.

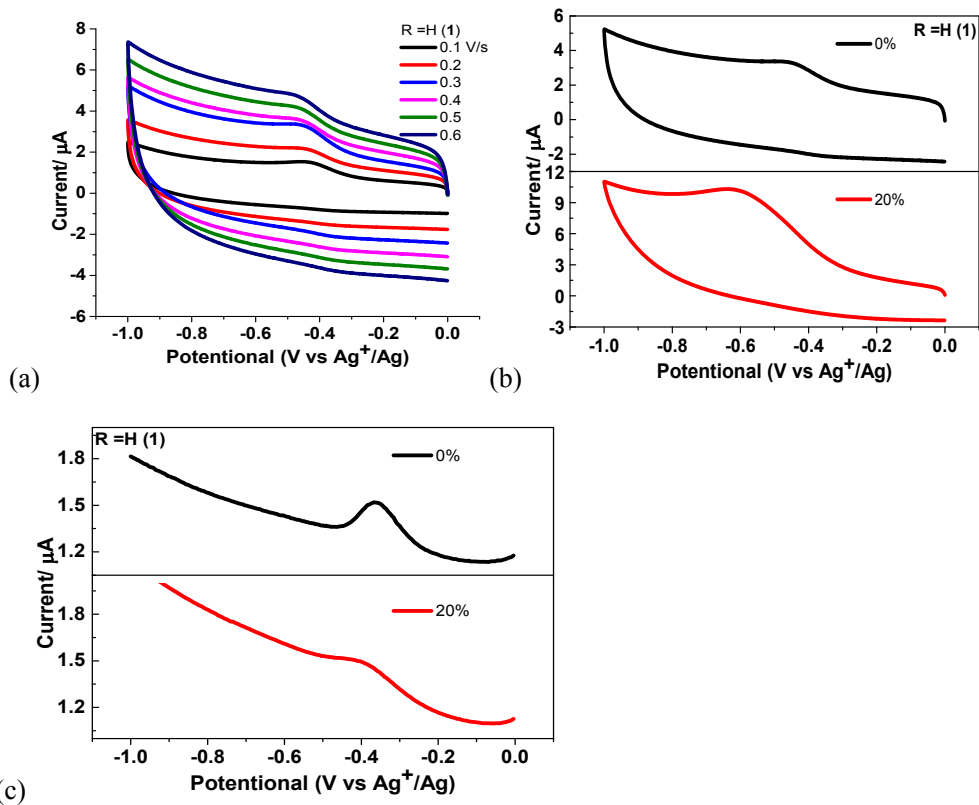


Figure S5. Scan-rate dependent cyclic voltammogram of complex **1** ($10^{-5} \text{ mol L}^{-1}$) in DMF/0.05 mM NBu_4PF_6 referenced against Ag^+/Ag (a), comparison between CV of complex **1** ($10^{-5} \text{ mol L}^{-1}$) in DMF (black) and aqueous DMF (20% water fraction) at a scan rate of 300 mV s^{-1} (b) and DPV (c) in the different media.

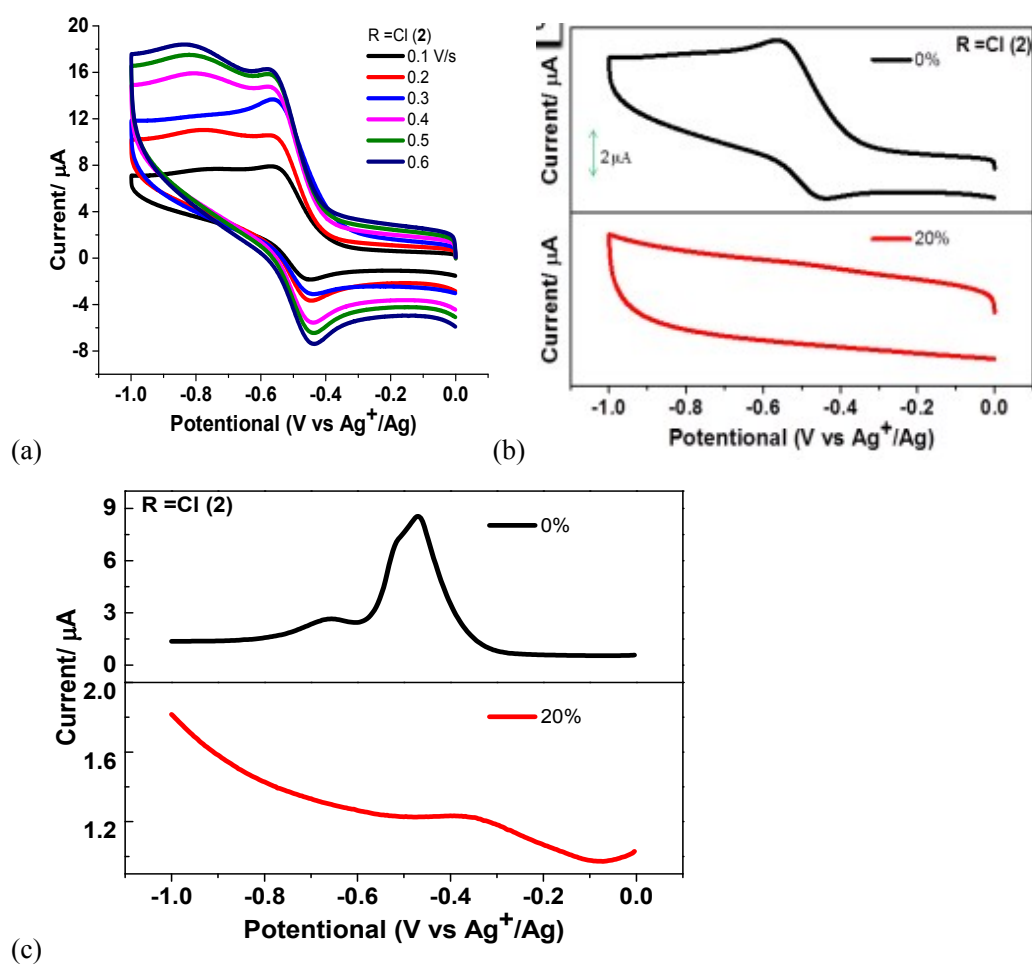


Figure S6. Scan-rate dependent cyclic voltammogram of complex 2 ($10^{-5} \text{ mol L}^{-1}$) in DMF/0.05 mM NBu_4PF_6 referenced against Ag^+/Ag , comparison between CV of complex 2 ($10^{-5} \text{ mol L}^{-1}$) in DMF (black) and aqueous DMF (20% water fraction) at a scan rate of 300 mV s^{-1} (b).

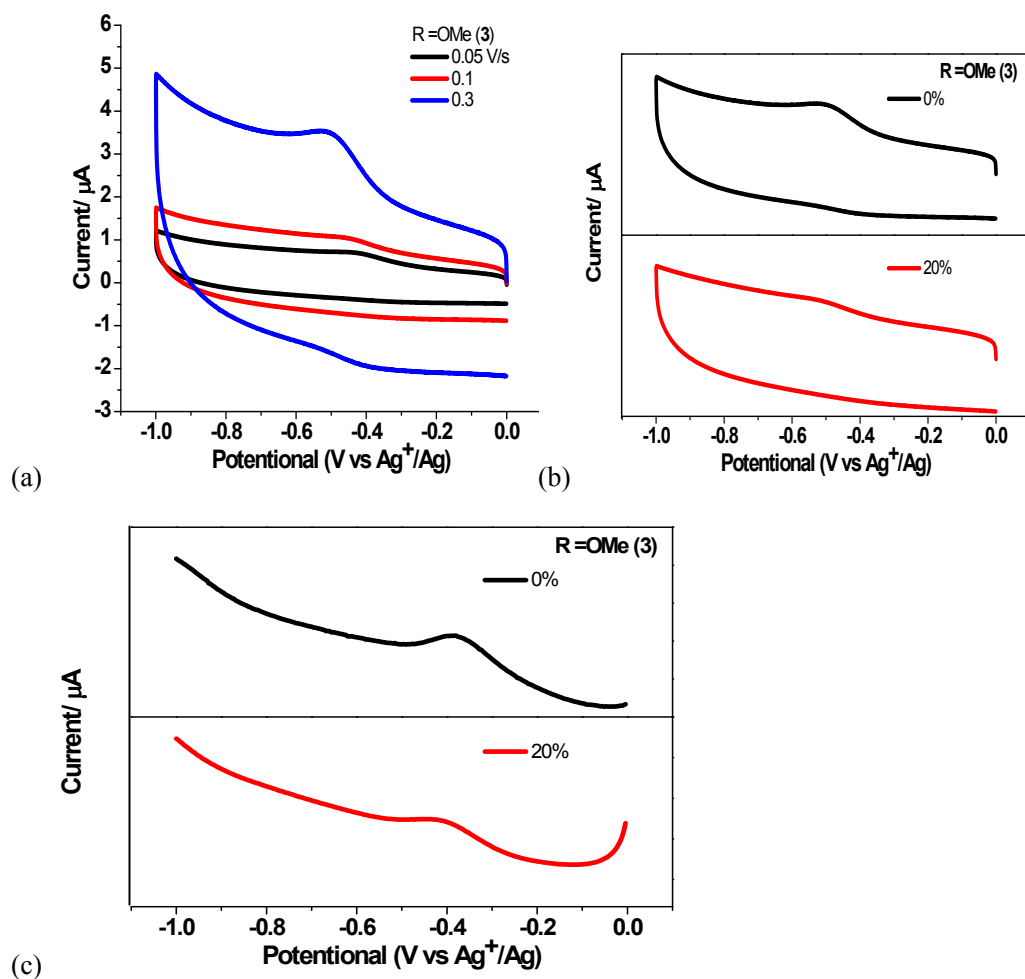


Figure S7. Scan-rate dependent cyclic voltammogram of complex **3** (10^{-5} mol L $^{-1}$) in DMF/0.05 mM NBu $_4$ PF $_6$ referenced against Ag $^+$ /Ag (a), comparison between CV of complex **6** (10^{-5} mol L $^{-1}$) in DMF (black) and aqueous DMF (20% water fraction) at a scan rate of 300 mV s $^{-1}$ (b) and DPV (c) in the different media.

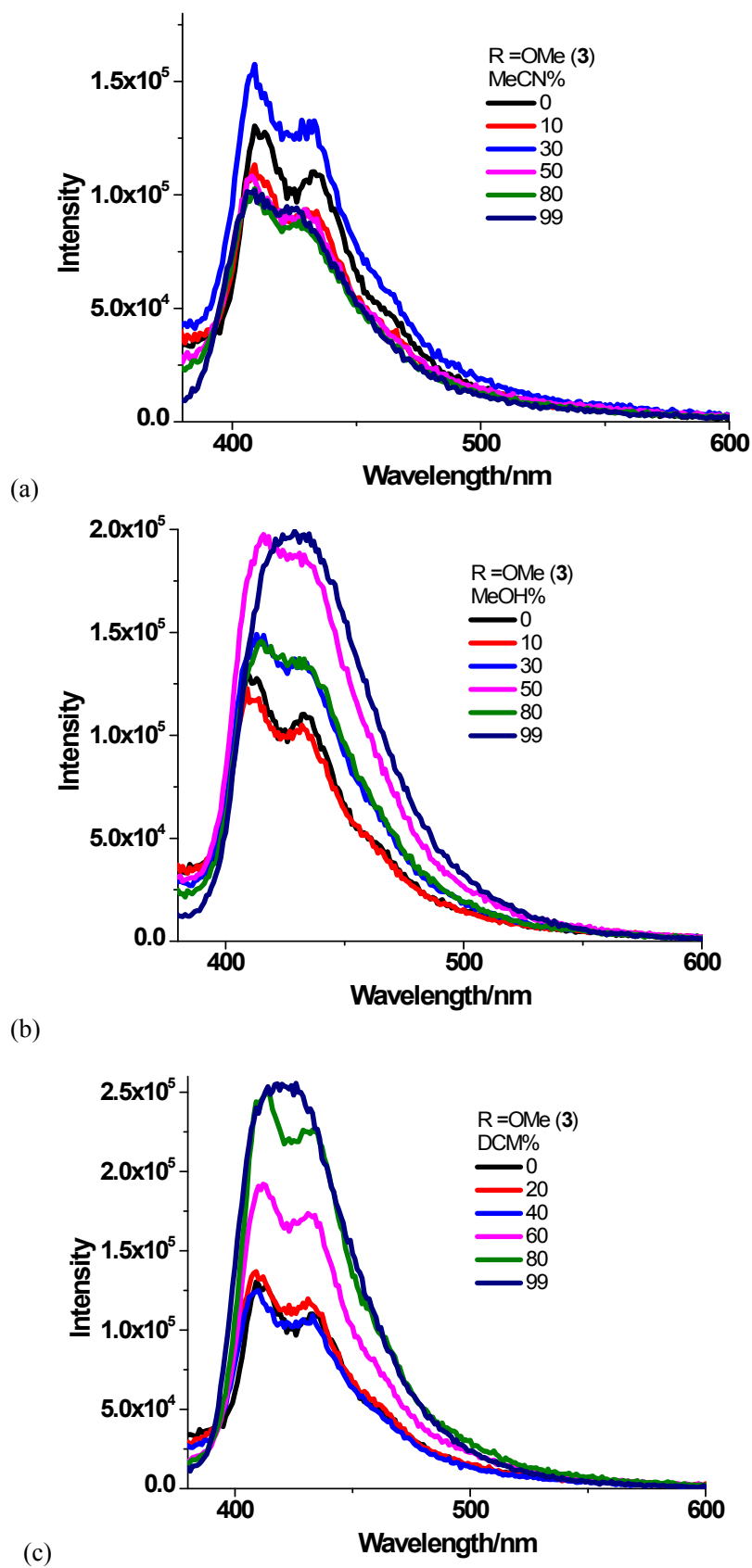
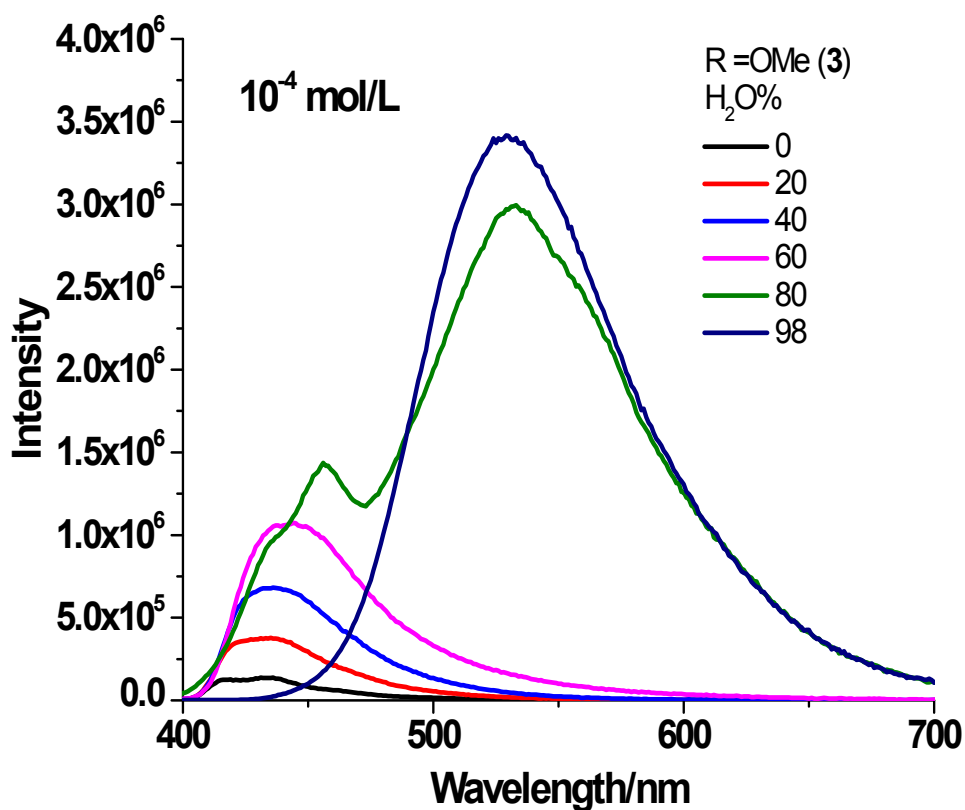
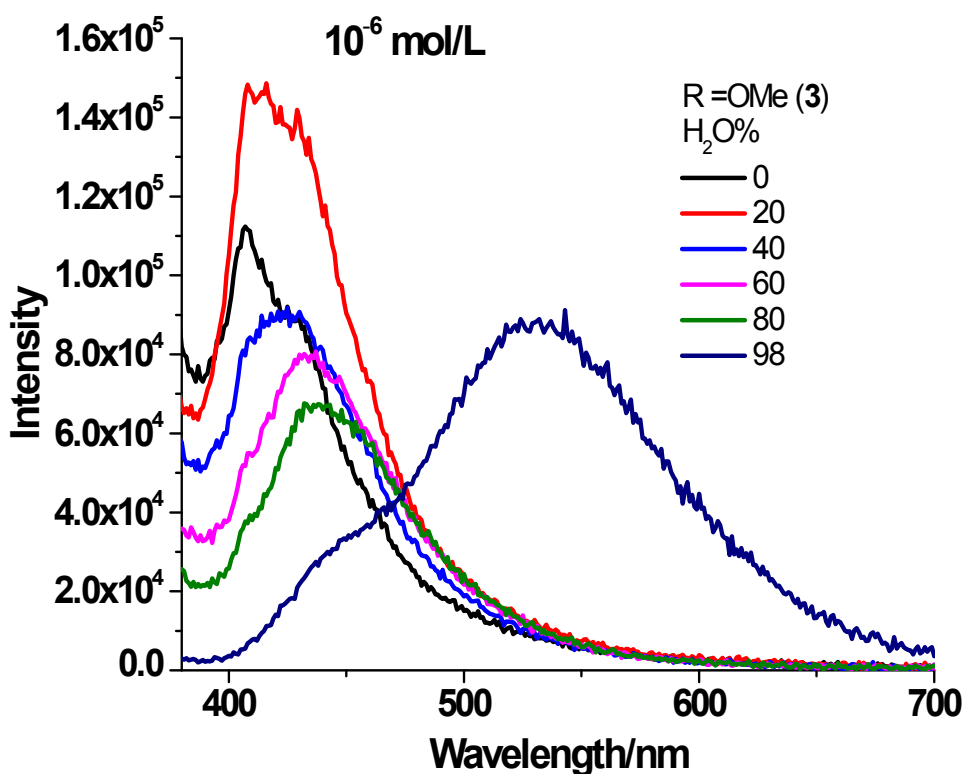


Figure S8. PL spectra of **3** in DMF/MeCN (A), DMF/MeOH (B) and DMF/CH₂Cl₂ mixtures with different volume fractions of cosolvent. $\lambda_{\text{ex}} = 365 \text{ nm}$, $C = 10 \text{ } \mu\text{M}$.



(A)



(B)

Figure S9. PL spectra of **3** in DMF/H₂O mixtures with different volume water fractions. $\lambda_{\text{ex}} = 365$ nm, $C = 100 \mu\text{M}$ (A) and $C = 1 \mu\text{M}$ (B).

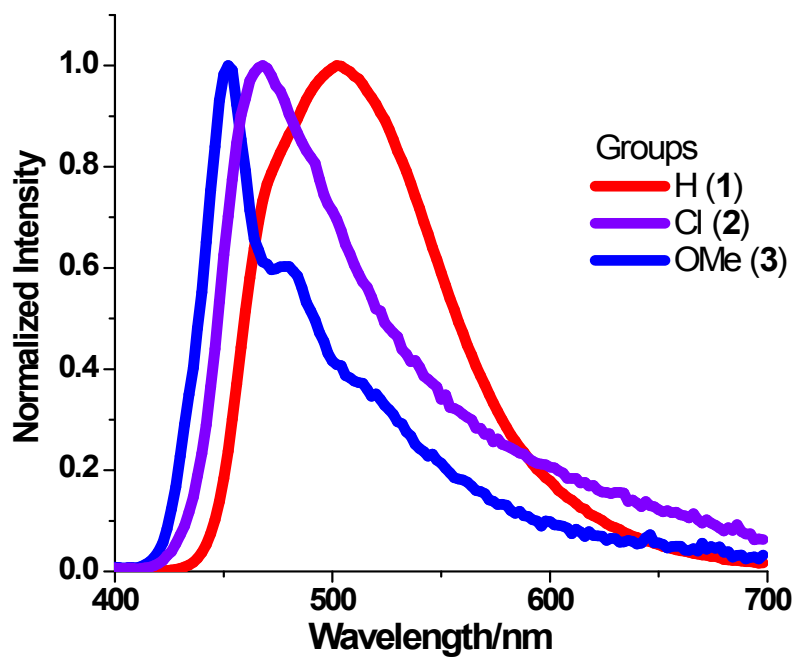


Figure S10. PL spectra of **1-3** in solid state, $\lambda_{\text{ex}} = 365$ nm.

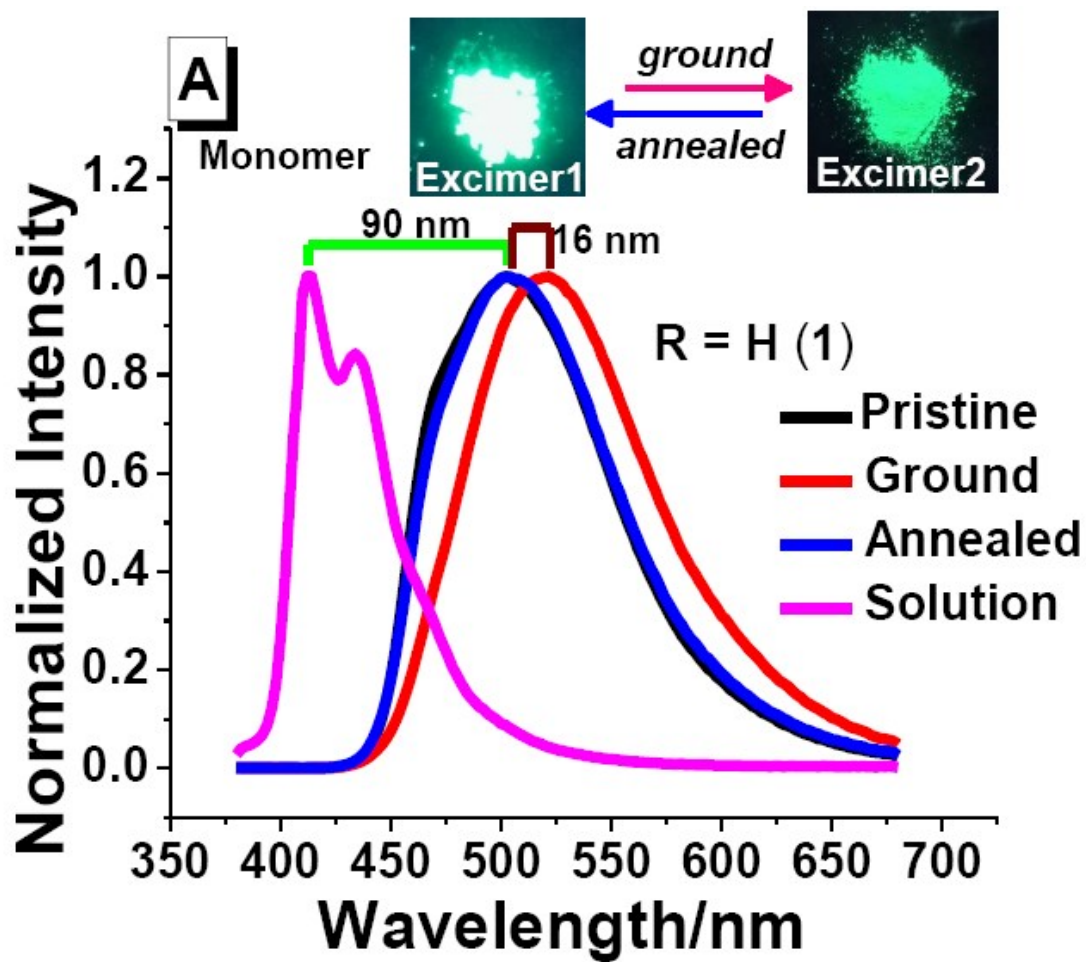


Figure. S11 Multistate emission spectra of compound **1** in diluted solution, pristine, ground and annealed solids and the photographs taken under 365 nm UV illumination

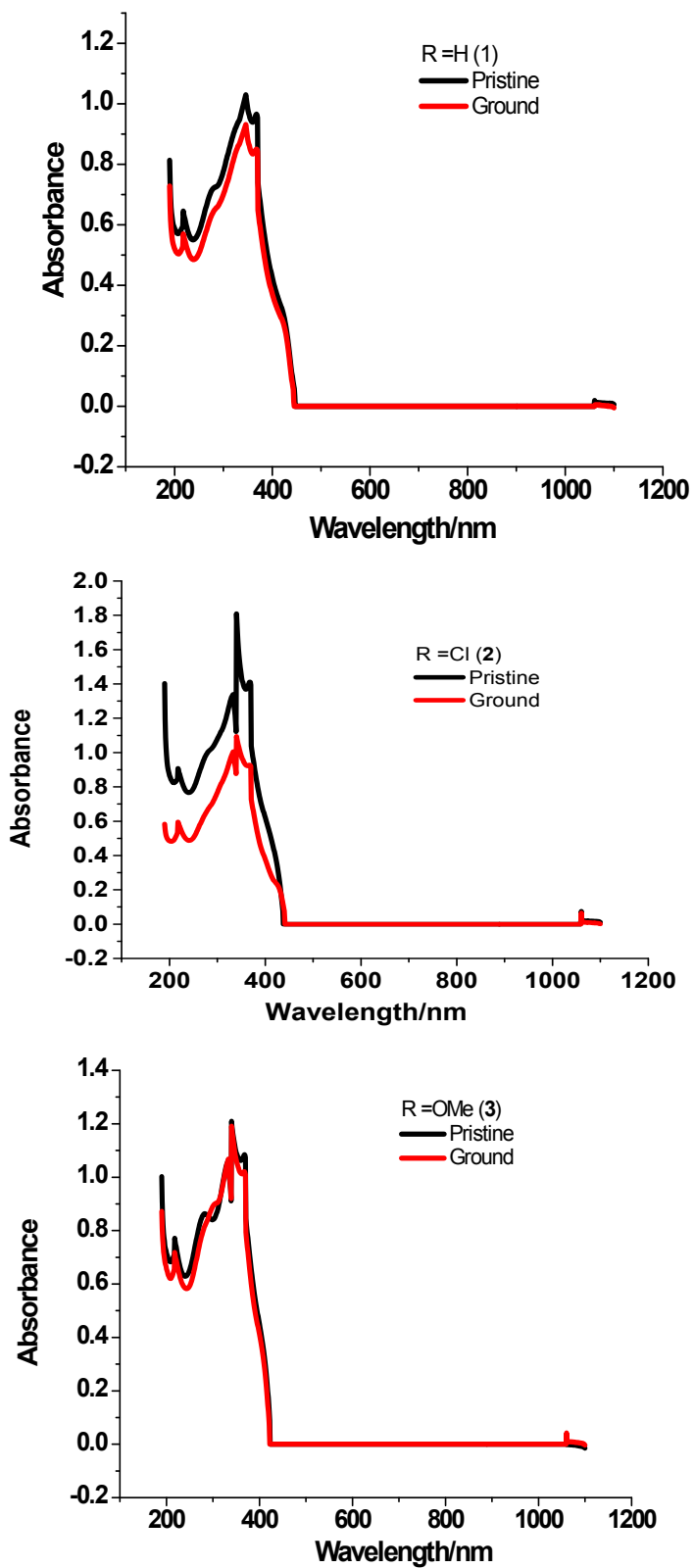


Figure S12. UV-vis spectra of pyrenyl-containing carbohydrozone derivatives in solid state.

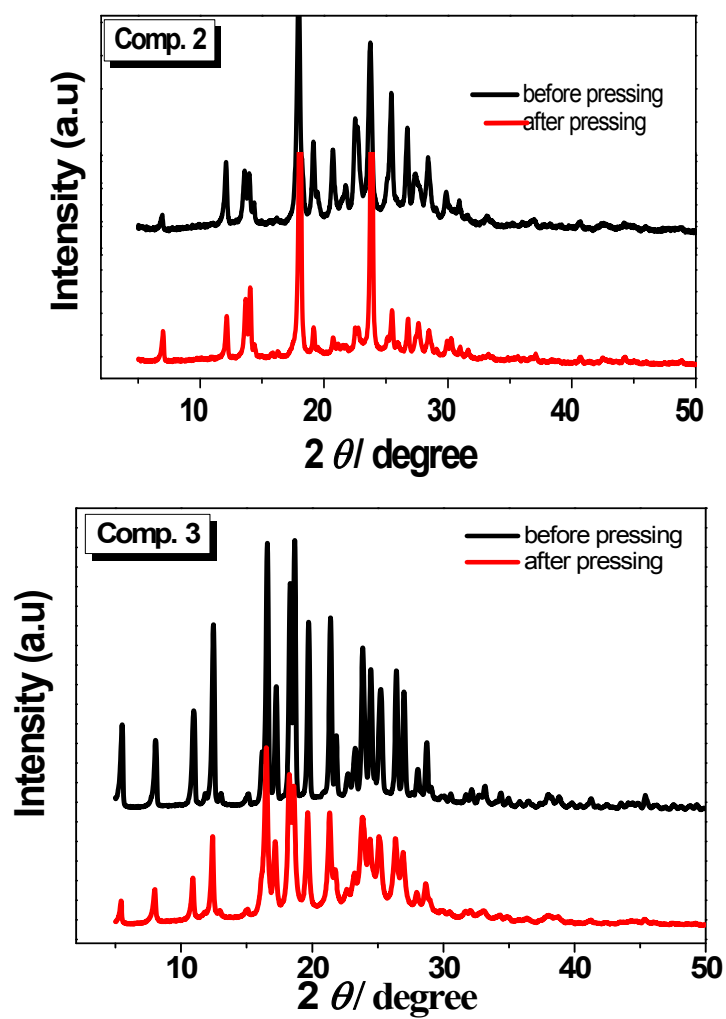


Figure S13. Powder XRD pattern of compound 2 and 3 before(black) and after grinding(red).

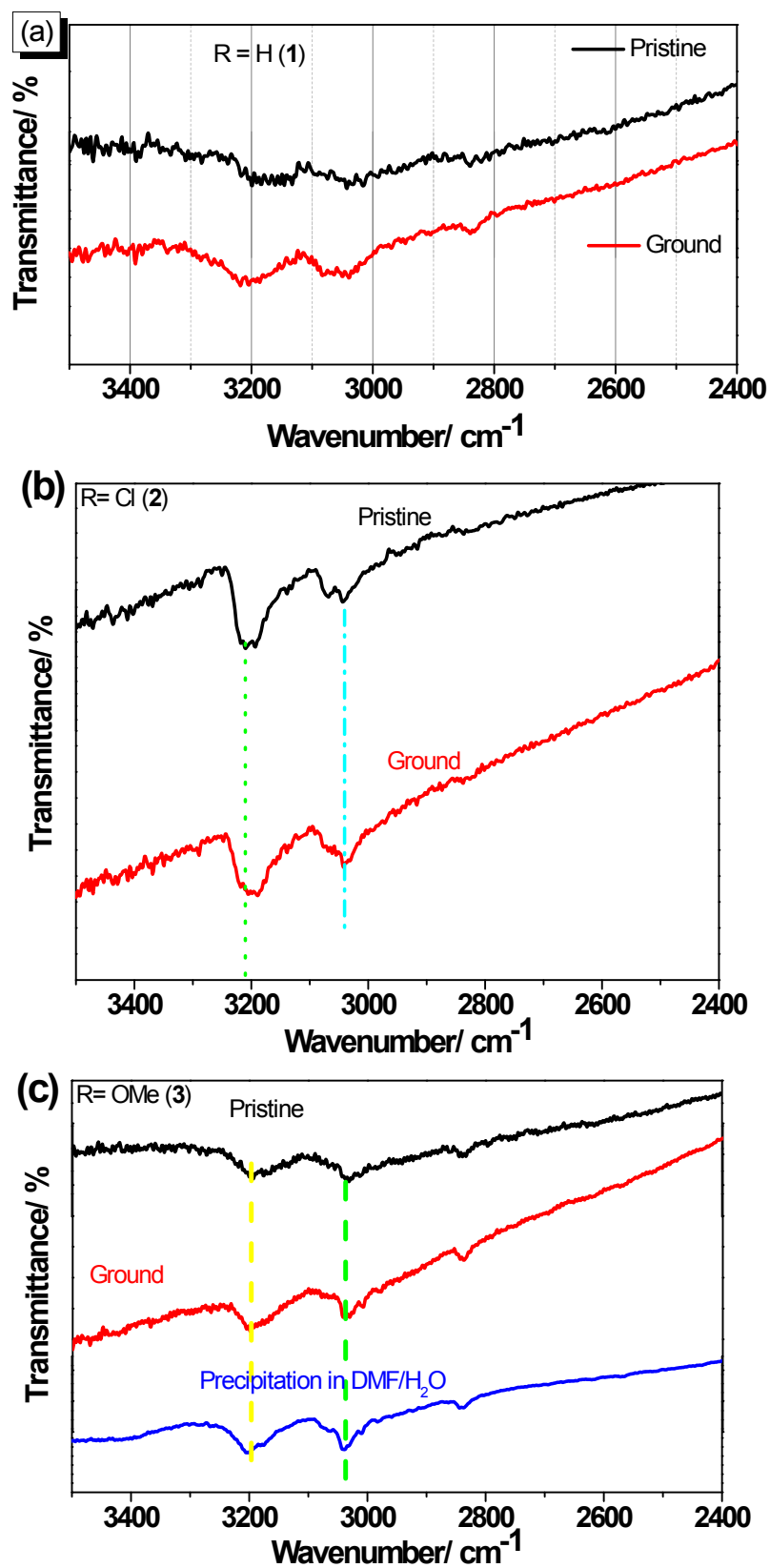


Figure S14. FT-IR spectra of compound 1-3 before(black) and after grinding(red).

Reference:

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