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Table S1. Selected bond lengths (Å) and angles (°) for 1·xSol.

Ag1–Ag2	3.3076(5)	S1–Ag1–S2	99.57(3)
Ag1–S1	2.6388(10)	S1–Ag1–Ag2	50.71(2)
Ag1–S2	2.5856(10)	S1–Ag2–S2	99.93(3)
Ag1–P1	2.4667(10)	S1–Ag2–Ag1	51.29(2)
Ag1–P2	2.4723(10)	S2–Ag1–Ag2	50.41(2)
Ag2–S1	2.6173(10)	S2–Ag2–Ag1	50.21(2)
Ag2–S2	2.5932(10)	P1–Ag1–Ag2	117.15(3)
Ag2–P3	2.4552(11)	P2–Ag1–Ag2	140.88(3)
Ag2–P4	2.4716(10)	P3–Ag2–Ag1	116.76(3)
		P4–Ag2–Ag1	141.04(3)

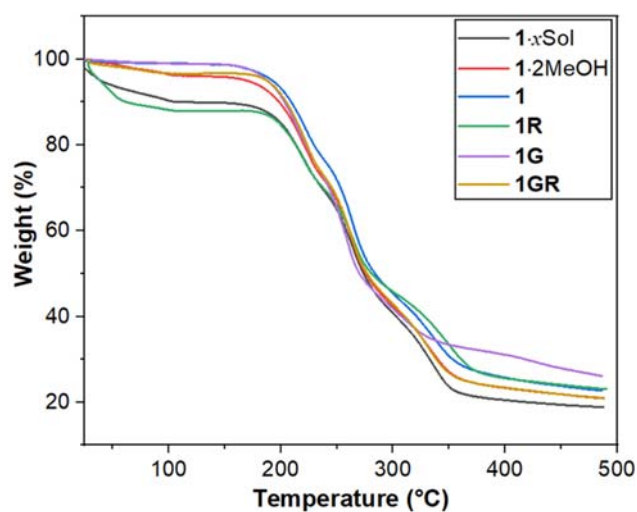


Figure S1. TGA curves of 1·xSol, 1·2MeOH, 1, 1R, 1G and 1GR under a N₂ atmosphere.

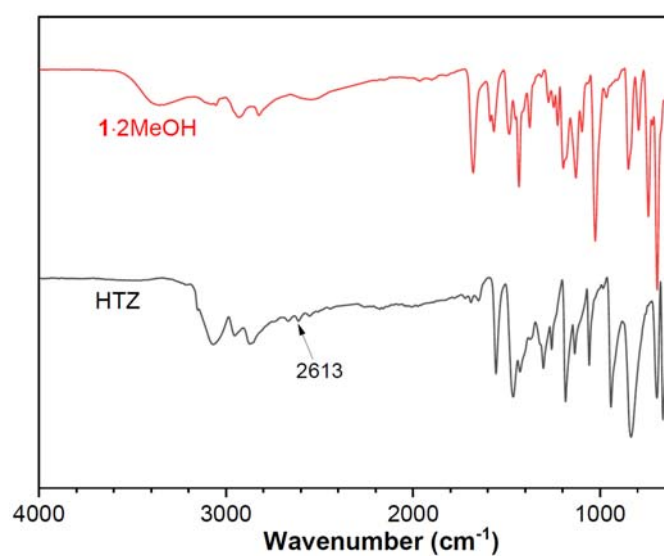


Figure S2. IR spectra of 1·2MeOH (red) and HTZ (black).

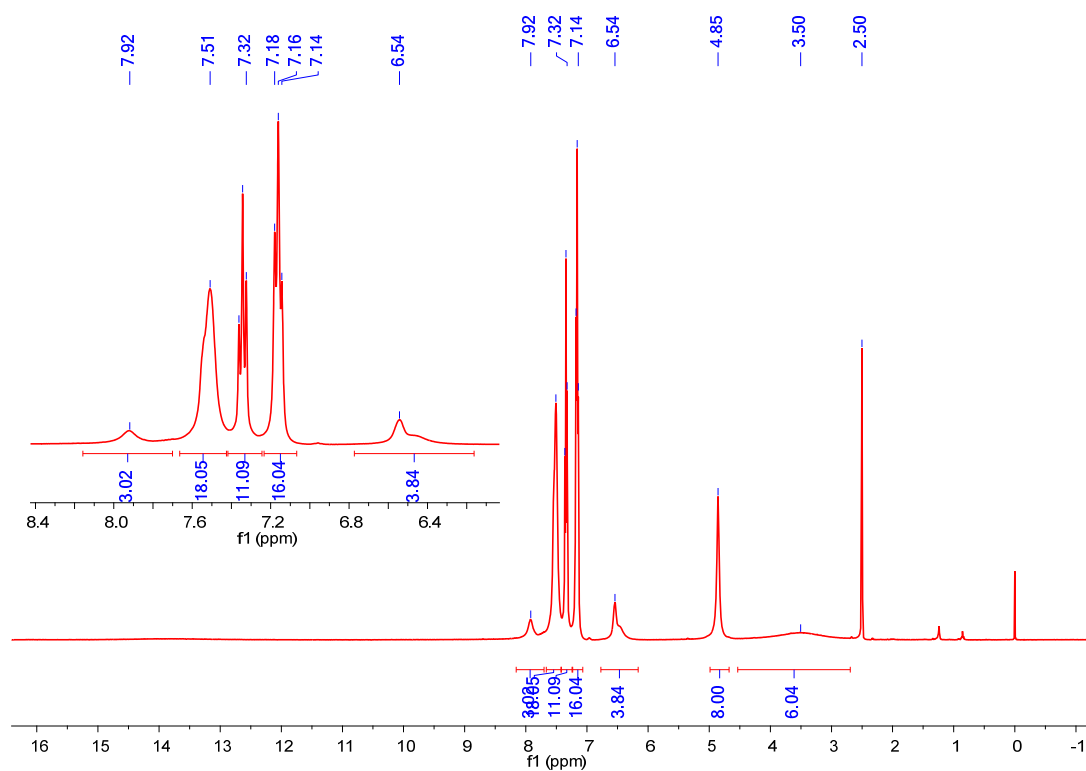


Figure S3. ¹H NMR spectrum of 1:2MeOH.

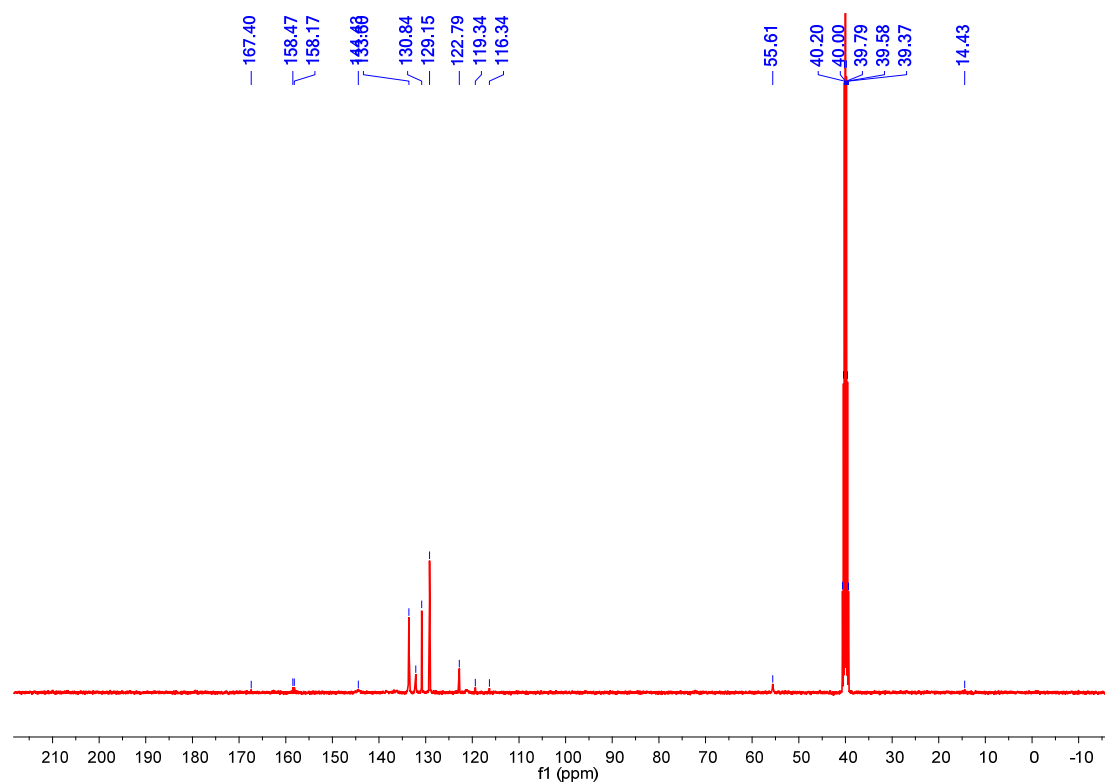


Figure S4. ¹³C NMR spectrum of 1:2MeOH

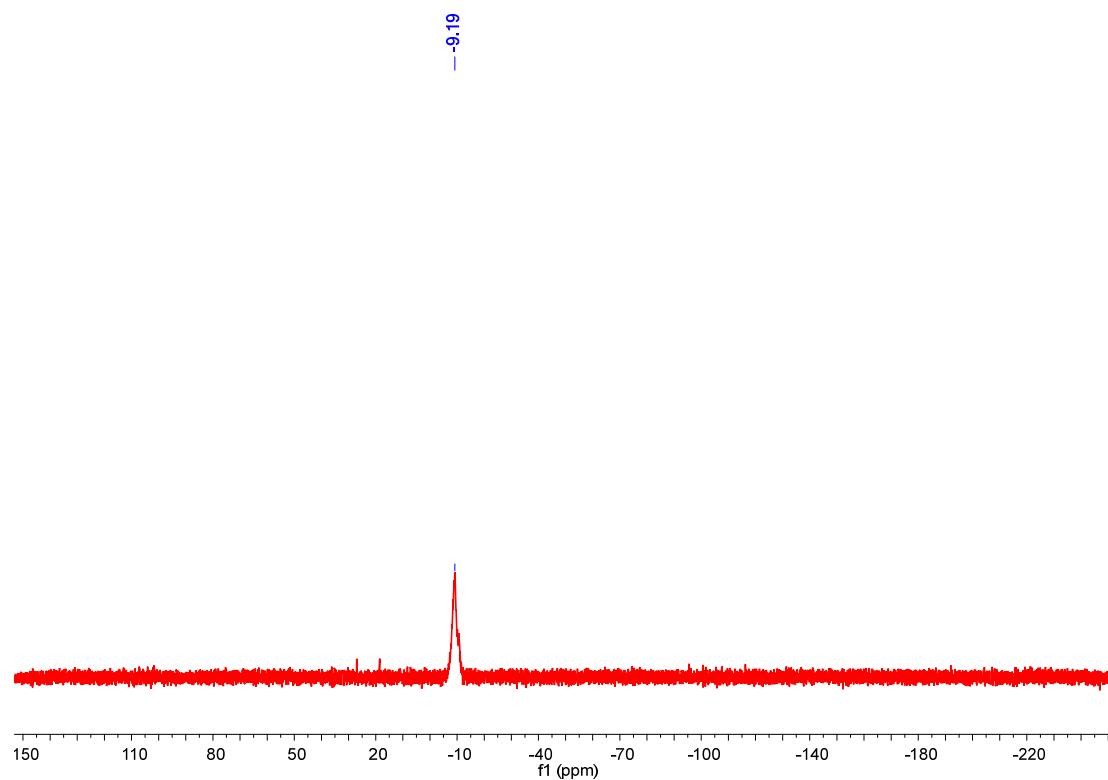


Figure S5. ^{31}P NMR spectrum of **1**·2MeOH

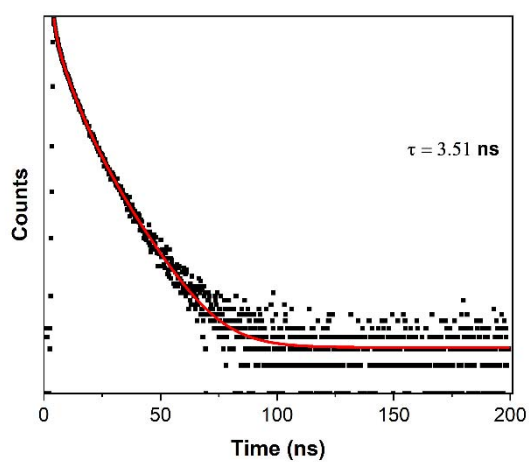


Figure S6. Transient photoluminescent data for **1**·xSol ($\lambda_{\text{ex}} = 373 \text{ nm}$) at ambient temperature.

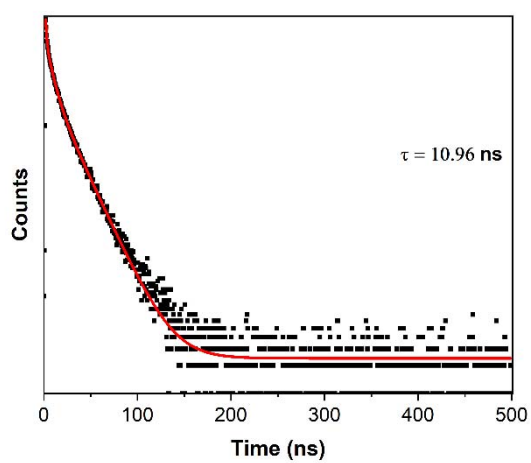


Figure S7. Transient photoluminescent data for 1:2MeOH ($\lambda_{ex} = 373 \text{ nm}$) at ambient temperature.

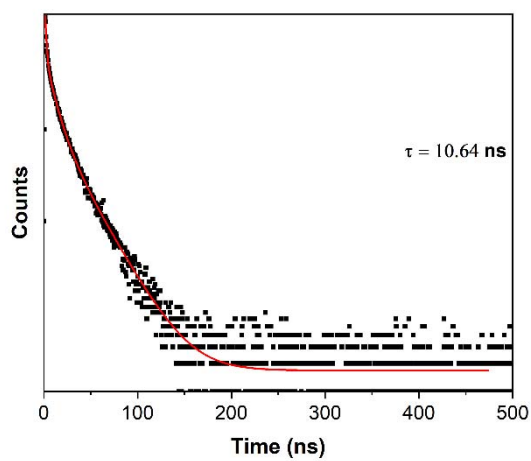


Figure S8. Transient photoluminescent data for **1** ($\lambda_{ex} = 373 \text{ nm}$) at ambient temperature.

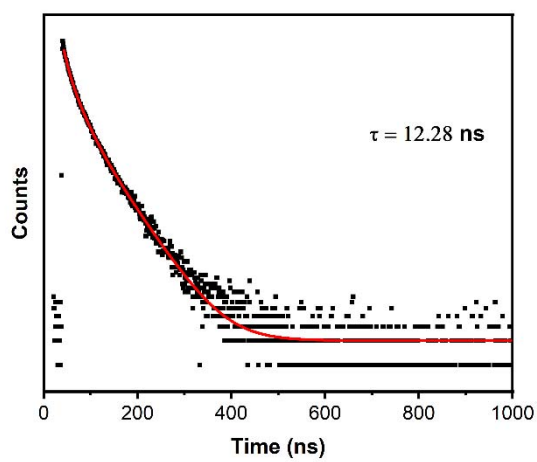


Figure S9. Transient photoluminescent data for 1:2MeOH ($\lambda_{ex} = 373 \text{ nm}$, $\lambda_{em} = 465 \text{ nm}$) at 80 K.

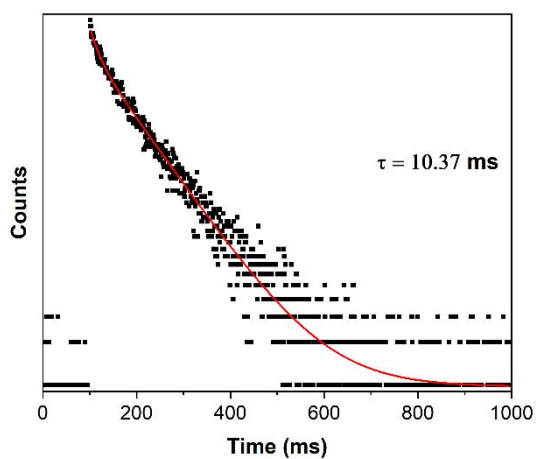


Figure S10. Transient photoluminescent data for 1·2MeOH ($\lambda_{ex} = 373$ nm, $\lambda_{em} = 516$ nm) at 80 K.

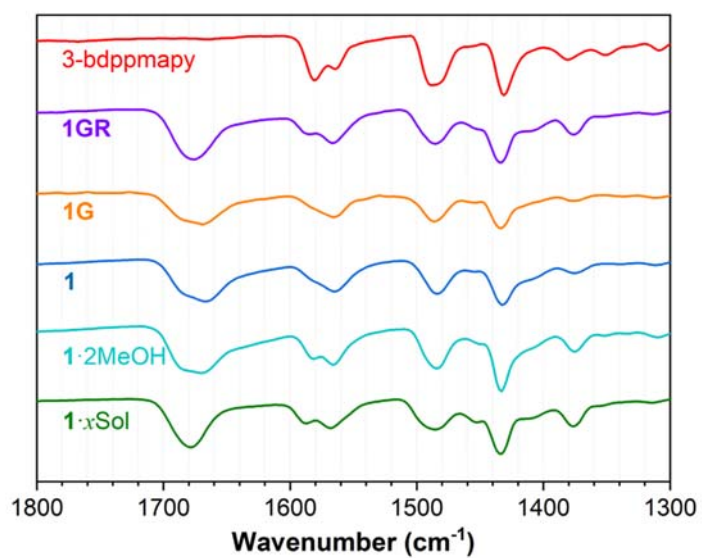


Figure S11. IR spectra of 1·xSol, 1·2MeOH, 1, 1G, 1GR and 3-bdppmapy in the region of 1800-1300 cm^{-1} .

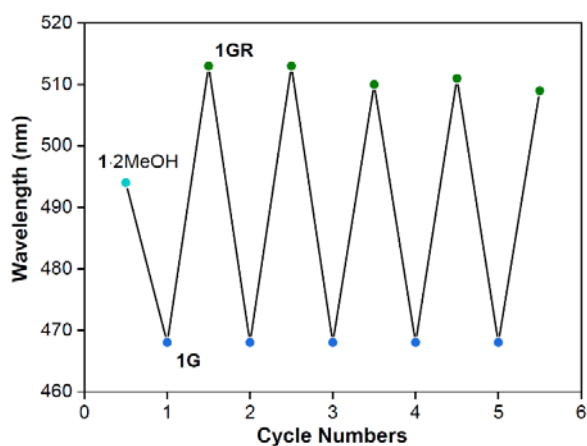


Figure S12. Emission wavelength of 1G/1GR upon exposure to MeOH vapor and grinding over five cycles.

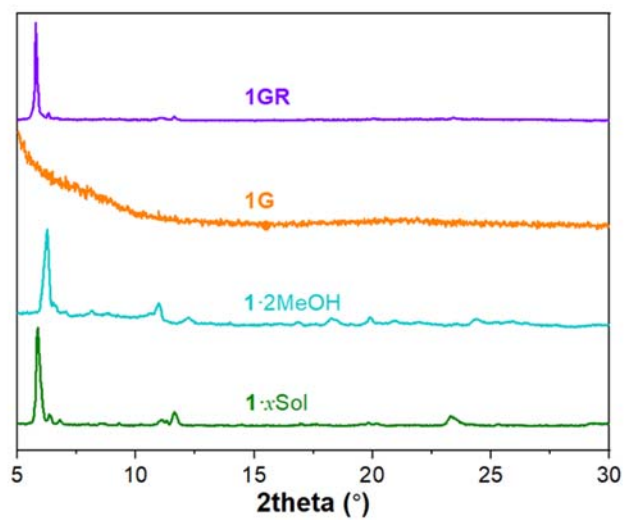


Figure S13. PXRD patterns for 1:χSol, 1:2MeOH, 1G and 1GR.