Electronic Supporting Information

Palladium-Catalyzed Polyannulation of Pyrazoles and Diynes toward Multifunctional Poly(indazole)s under Monomer Non-Stoichiometric Conditions

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320 nm. (B) Plot of relative emission intensity (I/I_0) versus the water fraction of the THF/water mixtures of model compound **4**.

Figure S18. (A) Emission spectra of P**1/2a** in THF/water mixtures with different water fractions (f_w). Solution concentration: 10 μM; excitation wavelength: 310 nm. (B) Plot of relative emission intensity (I/I_0) versus the water fraction of the THF/water mixtures of P**1/2a**. Inset: fluorescent photographs of P**1/2a** in THF solution and THF/water mixture with 90% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.

Figure S19. Emission spectra of (A) P**1/2b** and (B) P**1/2c** in THF/water mixtures with water fractions (f_w) at 0% and 90%. Solution concentration: 10 μM; excitation wavelength: 310 nm.

Figure S20. (A) Emission spectra of P**1/2d** in THF/water mixtures with different water fractions (f_w). Solution concentration: 10 μM; excitation wavelength: 330 nm. (B) Plot of relative emission intensity (I/I_0) versus the water fraction of the THF/water mixtures of P**1/2d.** Inset: fluorescent photographs of P**1/2d** in THF solution and THF/water mixture with 90% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.

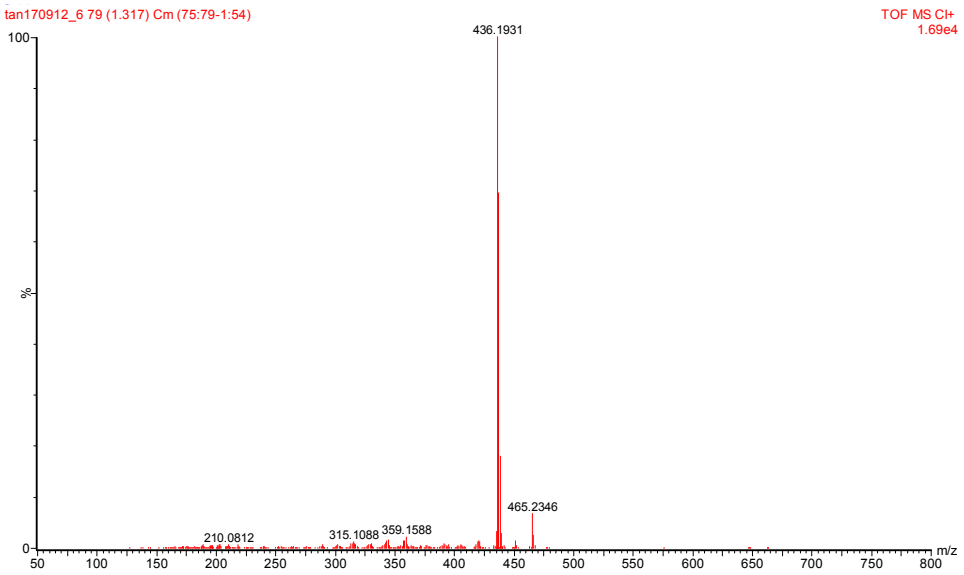


Figure S1. High-resolution mass spectra of model compound **4**.

Figure S2. High-resolution mass spectra of model compound **6**.

Table S1. Crystal data and structure refinement for **4**.

complex	**4**.
Empirical formula	$C_{32}H_{24}N_2$
Formula weight	436.53
Temperature	296.09(13) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	a = 12.7337(2) Å a= 90°. b = 14.4626(2) Å b= 90°. c = 13.1758(2) Å g = 90°.
Volume	2426.49(6) $Å^3$
Z	4
Density (calculated)	1.195 Mg/m^3
Absorption coefficient	0.534 mm^{-1}
F(000)	920
Theta range for data collection	4.540 to 71.160°.
Index ranges	-15<=h<=10, -17<=k<=14, -16<=l<=15
Reflections collected	6902
Independent reflections	3966 [R(int) = 0.0139]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.75628
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3966 / 109 / 298
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0947
R indices (all data)	R1 = 0.0390, wR2 = 0.0974
Absolute structure parameter	0.1(8)
Extinction coefficient	0.0037(3)
Largest diff. peak and hole	0.181 and -0.116 $e.Å^{-3}$

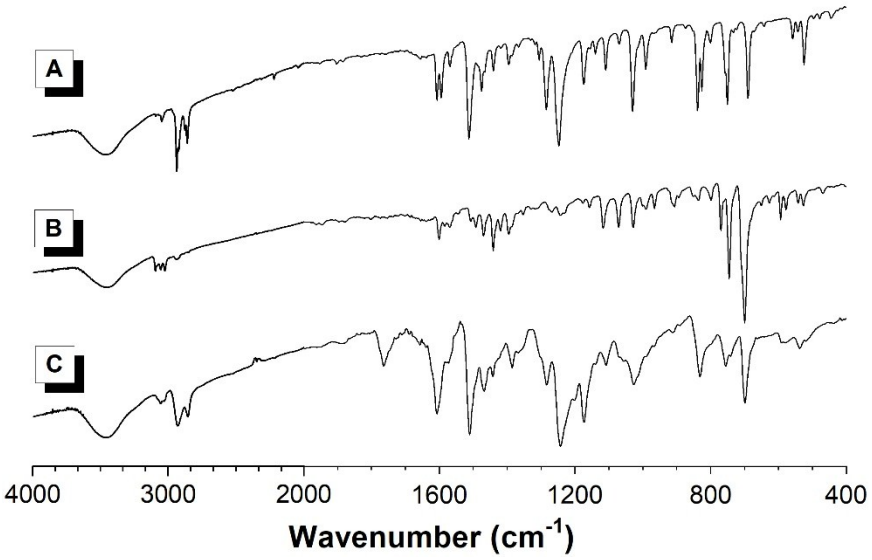


Figure S3. IR spectra of (A) **2a**, (B) model compound **4**, (C) P**1**/**2a**.

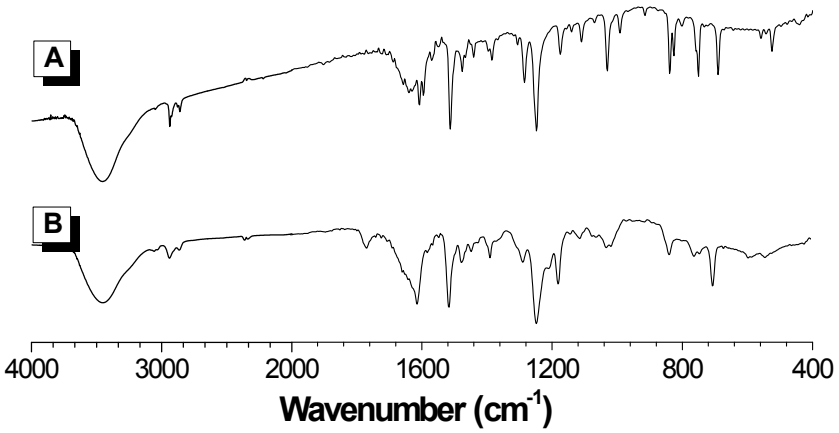


Figure S4. IR spectra of (A) **2b** and (B) P**1**/**2b**.

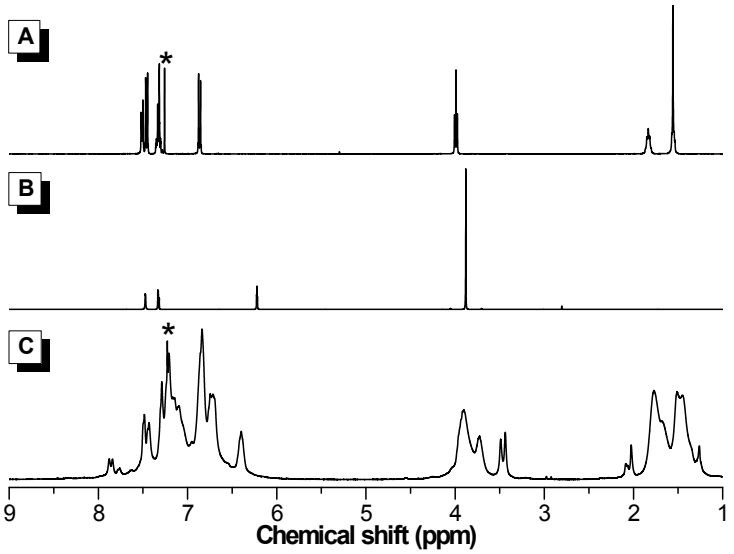


Figure S5. ^{11}H NMR spectra of (A) **2b** and (B) **1** and (C) P**1**/**2b** in chloroform-*d*. The solvent peaks were marked with asterisks.

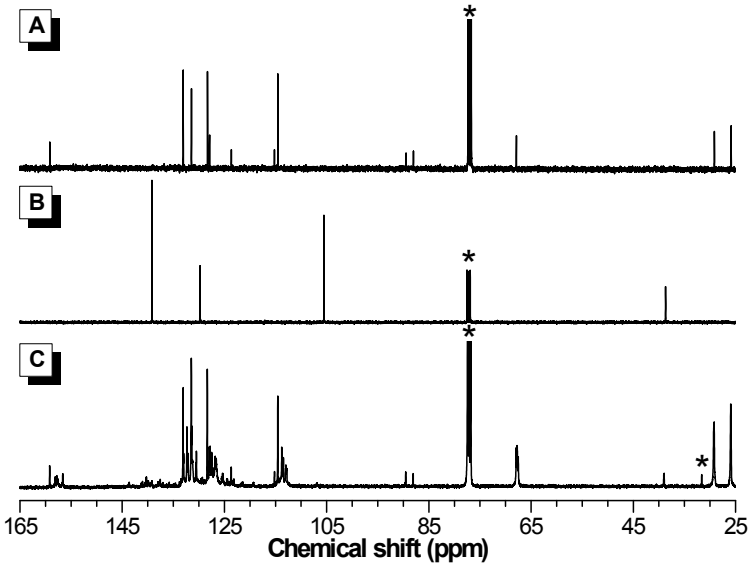


Figure S6. ^{13}C NMR spectra of (A) **2b**, (B) **1** and (C) P**1**/**2b** in chloroform-*d*. The solvent peaks were marked with asterisks.

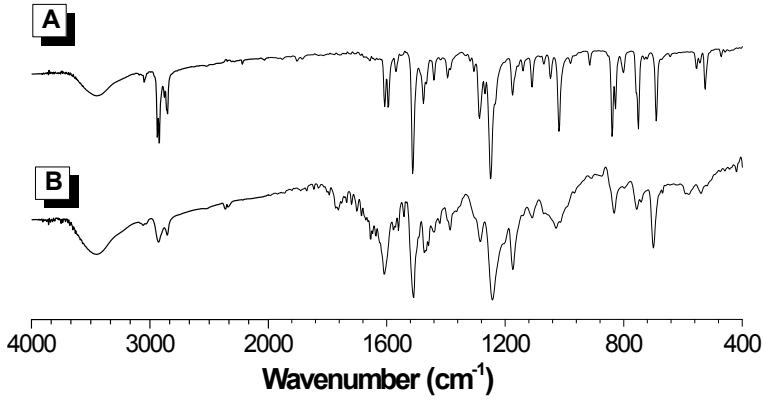


Figure S7. IR spectra of (A) **2c** and (B) P**1**/**2c**.

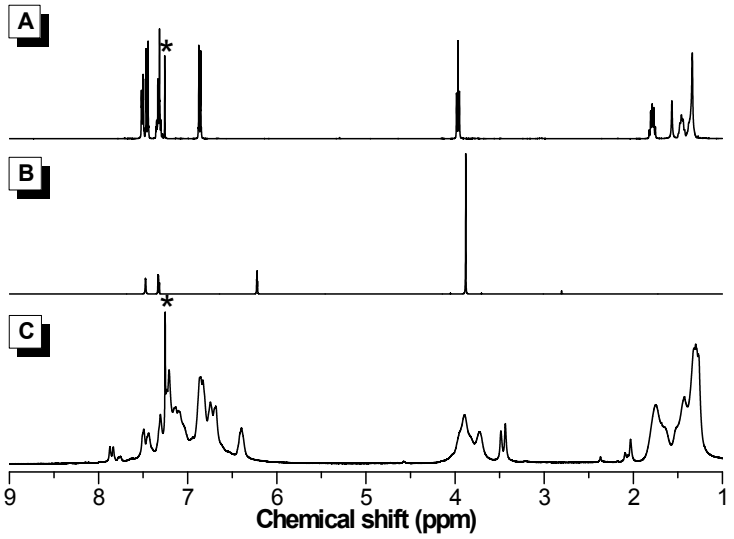


Figure S8. ^{11}H NMR spectra of (A) **2c** and (B) **1** and (C) P**1**/**2c** in chloroform-*d.* The solvent peaks were marked with asterisks.

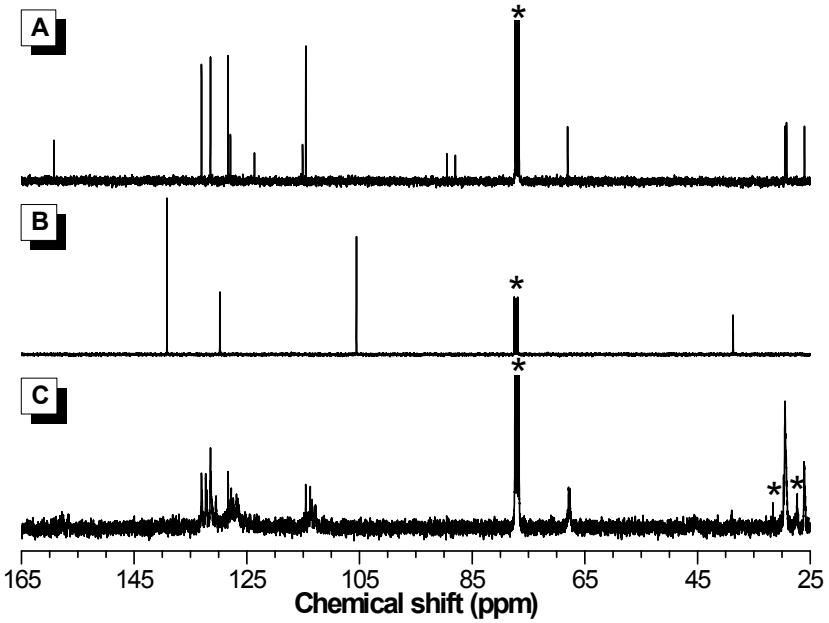


Figure S9. ^{13}C NMR spectra of (A) **2c** and (B) **1** and (C) P**1**/**2c** in chloroform-*d*. The solvent peaks were marked with asterisks.

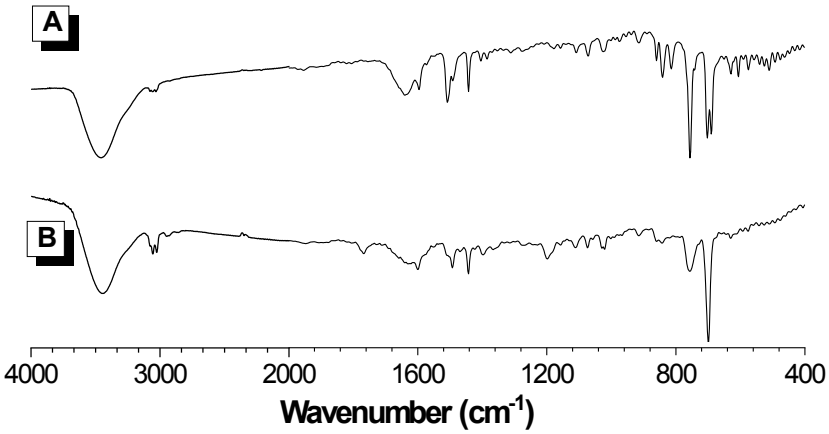


Figure S10. IR spectra of (A) **2d** and (B) P**1**/**2d**.

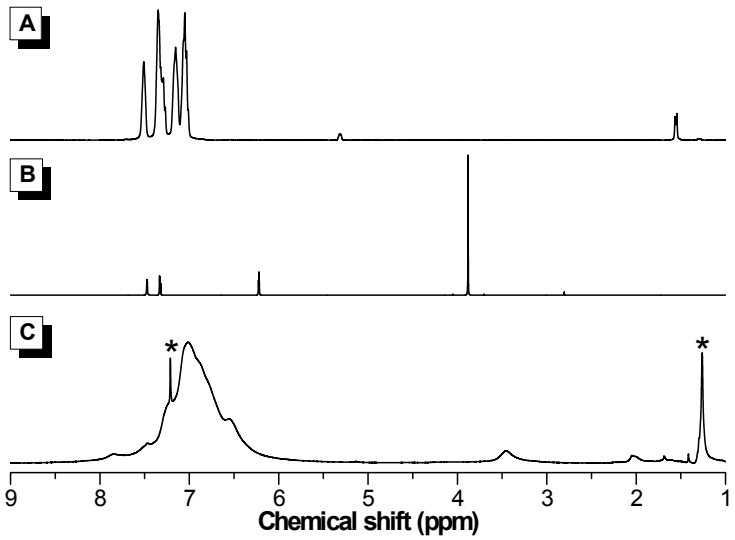


Figure S11. ^{11}H NMR spectra of (A) **2d** in dichloromethane-d_2 and chloroform-*d*, (B) **1** and (C) P**1**/**2d** in chloroform-*d*. The solvent peaks were marked with asterisks.

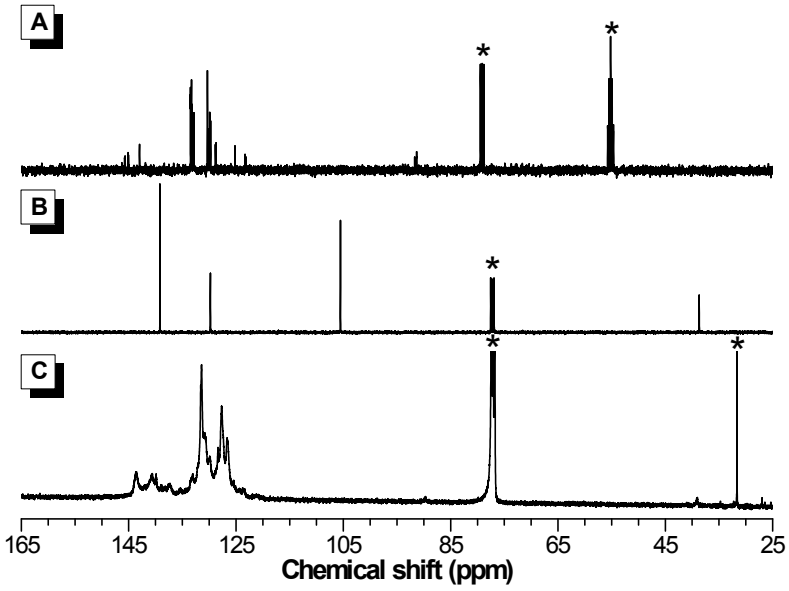


Figure S12. ^{13}C NMR spectra of (A) **2d** in dichloromethane-d_2 and chloroform-*d*, (B) **1** and (C) P**1**/**2d** in chloroform-*d*. The solvent peaks were marked with asterisks.

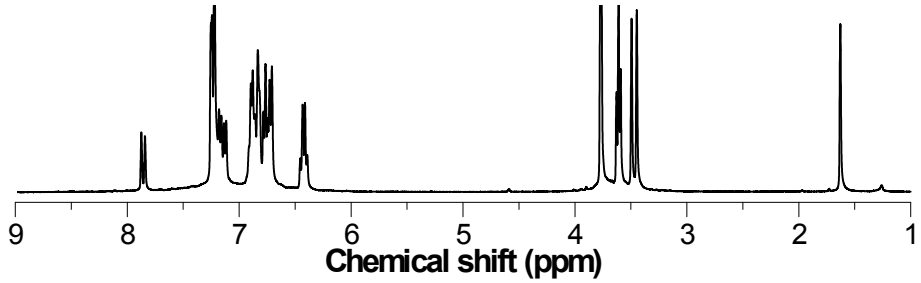


Figure S13. ^{1}H NMR spectra of **6** in chloroform-*d*.

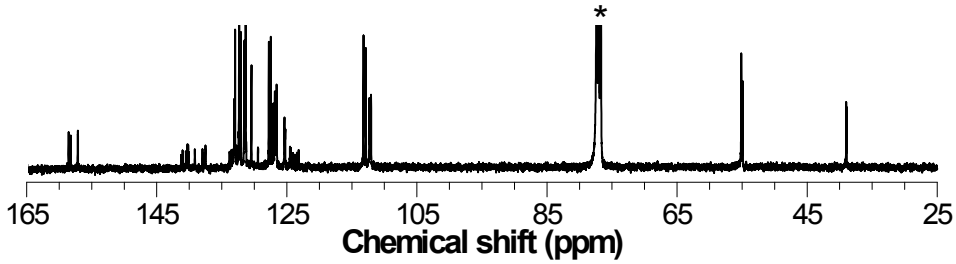


Figure S14. ^{13}C NMR spectra of **6** chloroform-*d*.

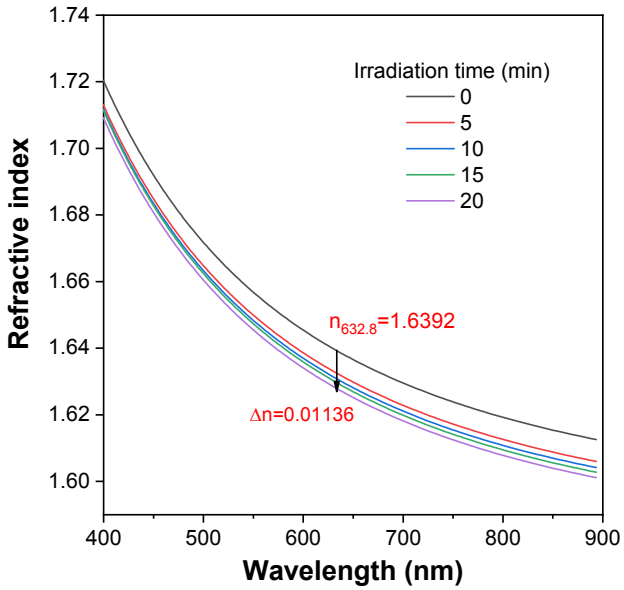


Figure S15. Wavelength dependence of the refractive index of a thin film of P**1**/**2a** on the UV irradiation time.

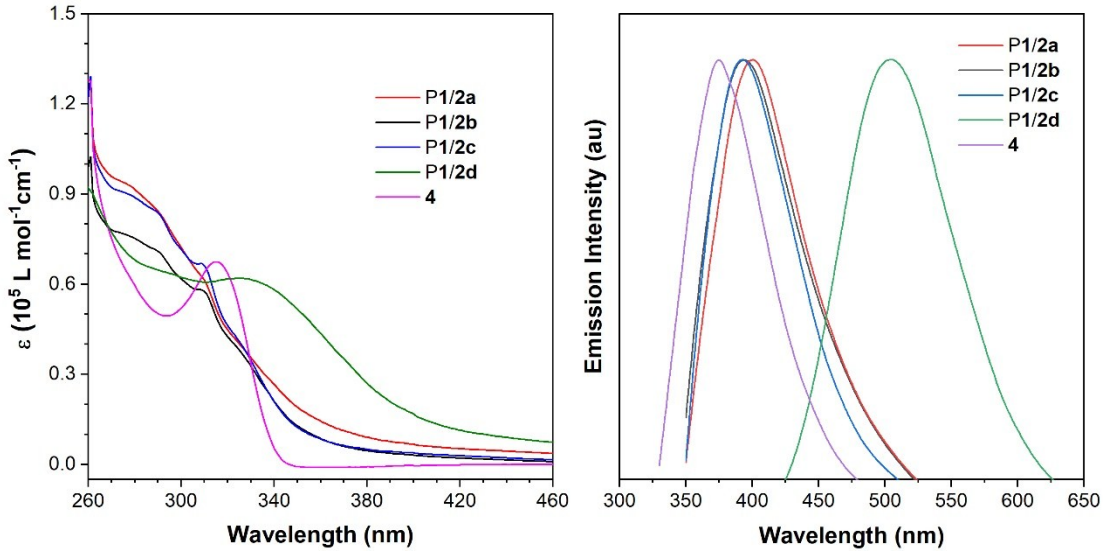


Figure S16. (A) Absorption spectra and (B) emission spectra of P**1/2** and **4** in THF solution. Solution concentration: 10 μM.

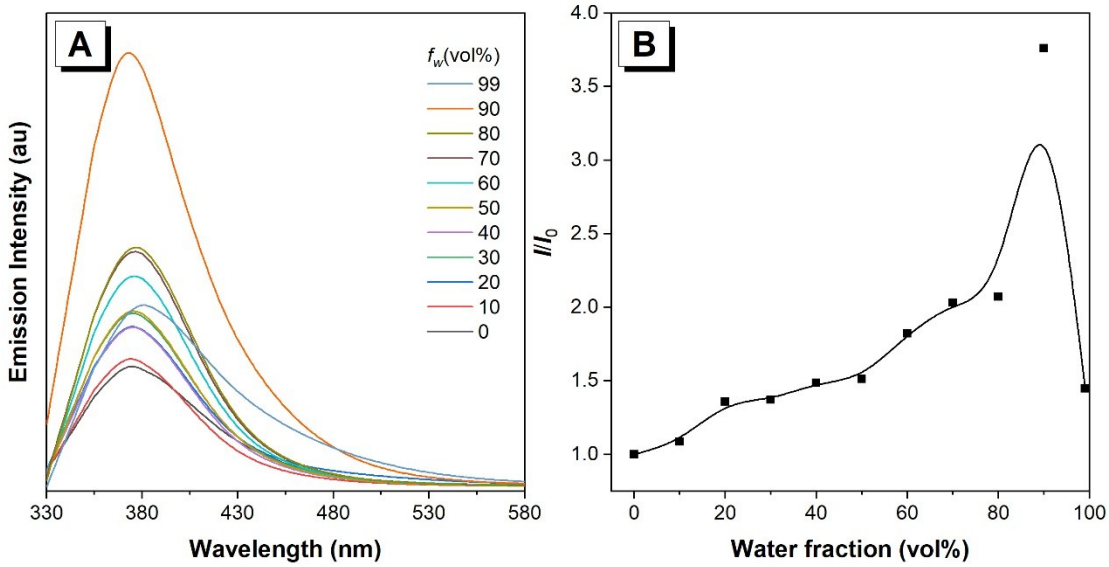


Figure S17. (A) Emission spectra of model compound **4** in THF/water mixtures with different water fractions (f_w). (Solution concentration: 10 μM; excitation wavelength: 320 nm). (B) Plot of relative emission intensity (I/I_0) versus the water fraction of the THF/water mixtures of model compound **4**.

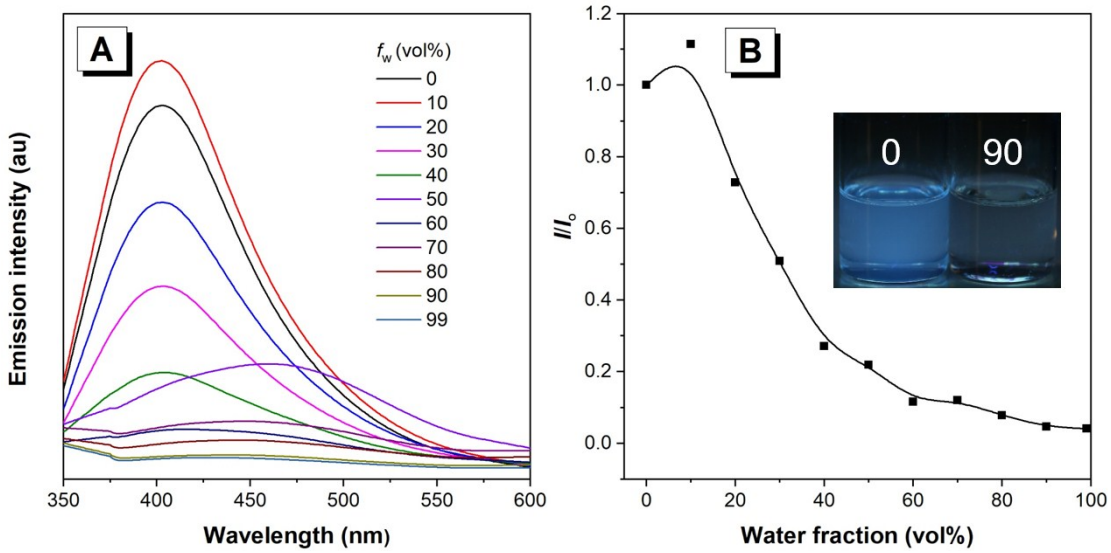


Figure S18. (A) Emission spectra of P**1**/**2a** in THF/water mixtures with different water fractions (f_w). (Solution concentration: 10 μM; excitation wavelength: 310 nm). (B) Plot of relative emission intensity (I/I_0) versus the water fraction of the THF/water mixtures of P**1**/**2a**. Inset: fluorescent photographs of P**1**/**2a** in THF solution and THF/water mixture with 90% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.

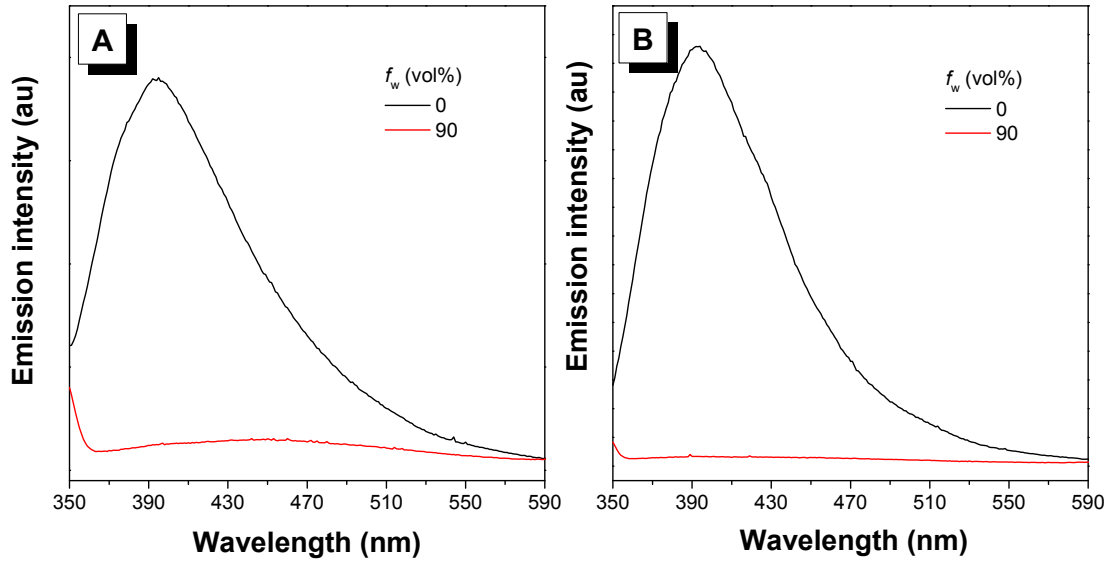
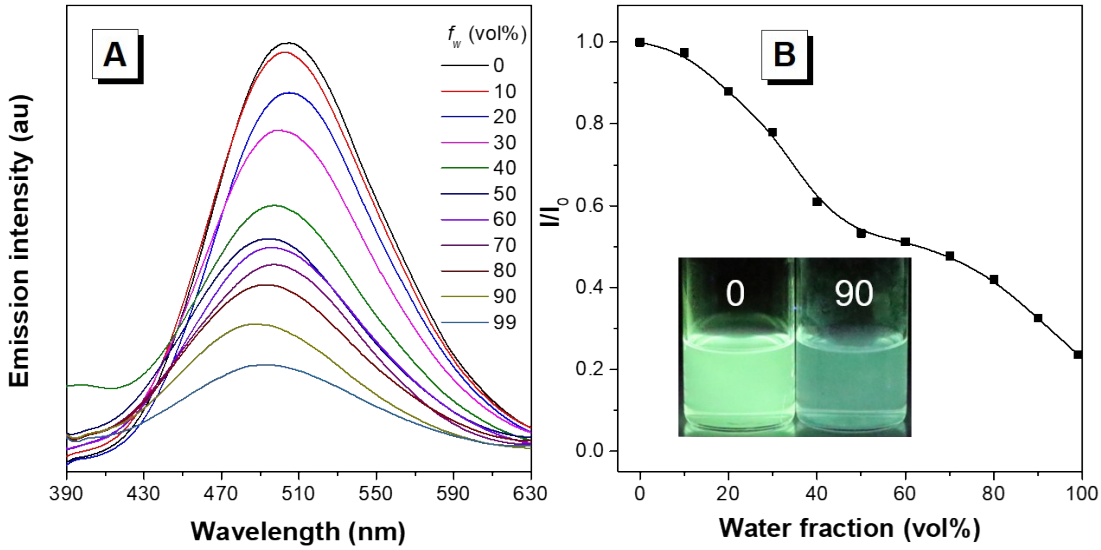


Figure S19. Emission spectra of (A) P**1**/**2b** and (B) P**1**/**2c** in THF/water mixtures with water fractions (f_w) at 0% and 90%. (Solution concentration: 10 μM; excitation wavelength: 310 nm).



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