

*Electronic Supporting Information*

BCl<sub>3</sub>-mediated polycoupling of alkyne and aldehyde: A facile,  
metal-free multicomponent polymerization route to  
stereoregular functional polymers

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Solution concentration: 10  $\mu$ M; excitation wavelength: 350 nm.

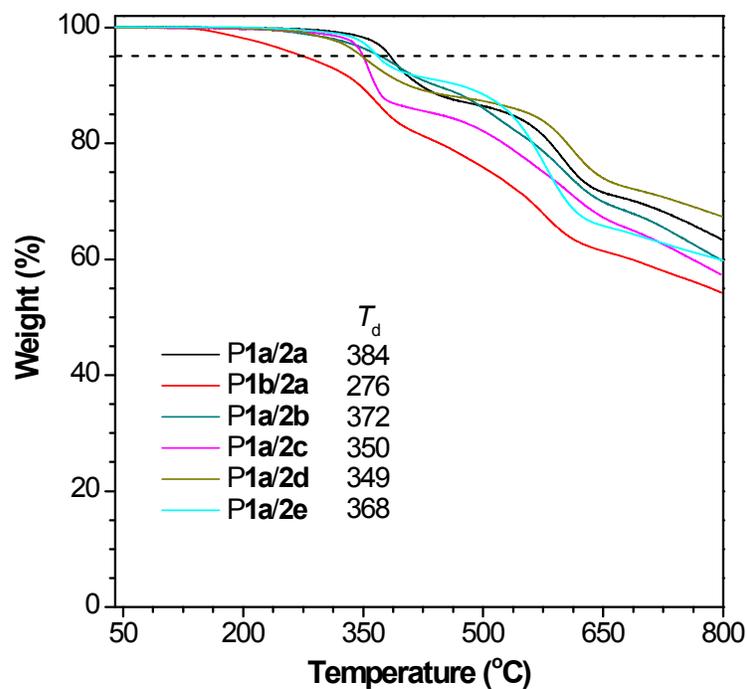


Fig. S1 TGA thermograms of P1/2 recorded under nitrogen at a heating rate of 10 °C/min.

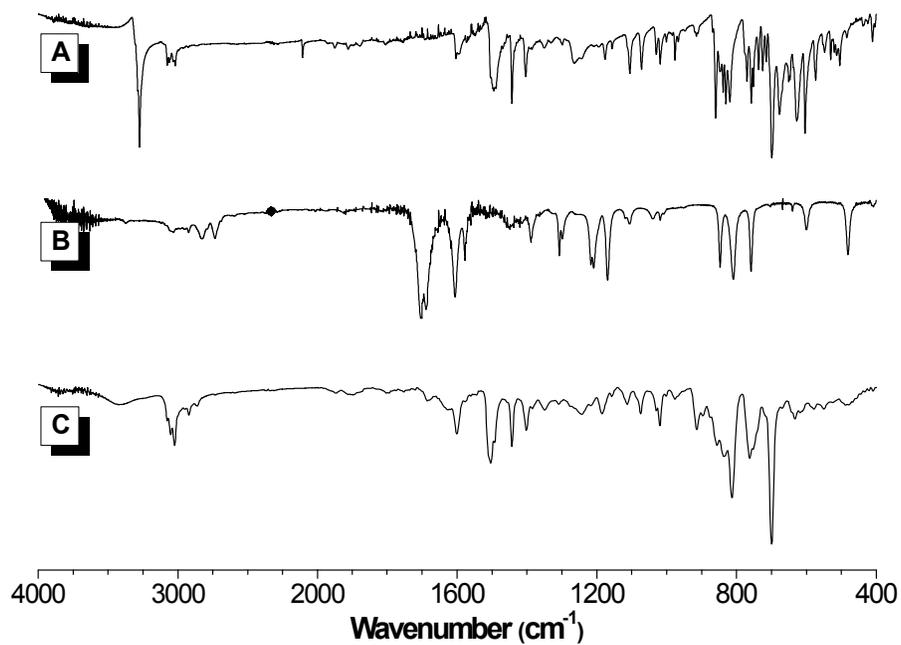
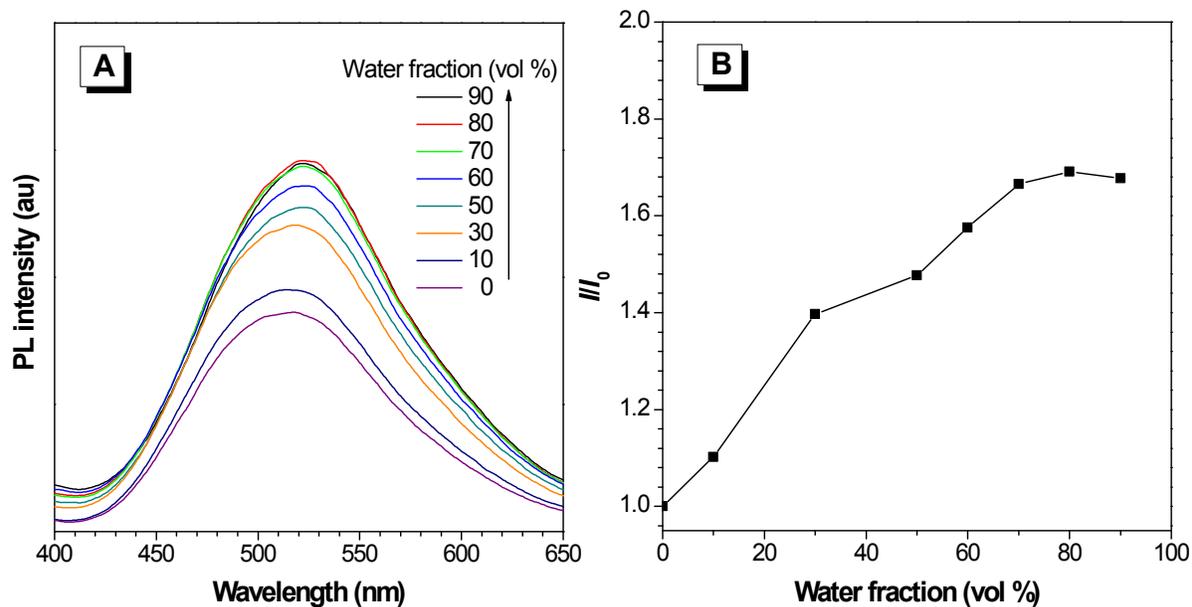
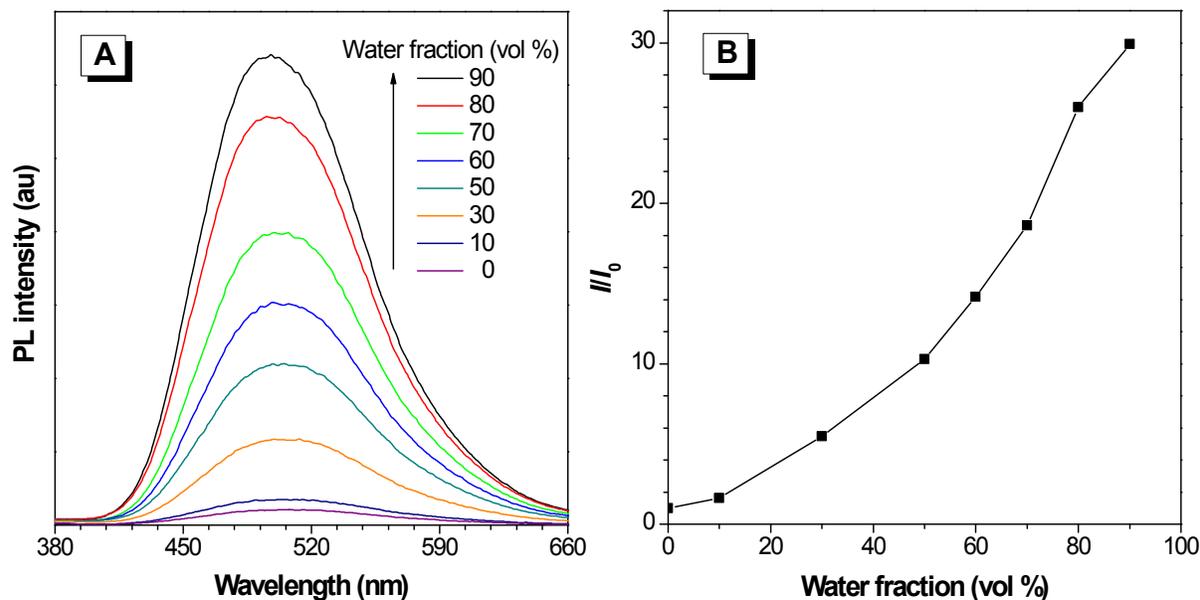


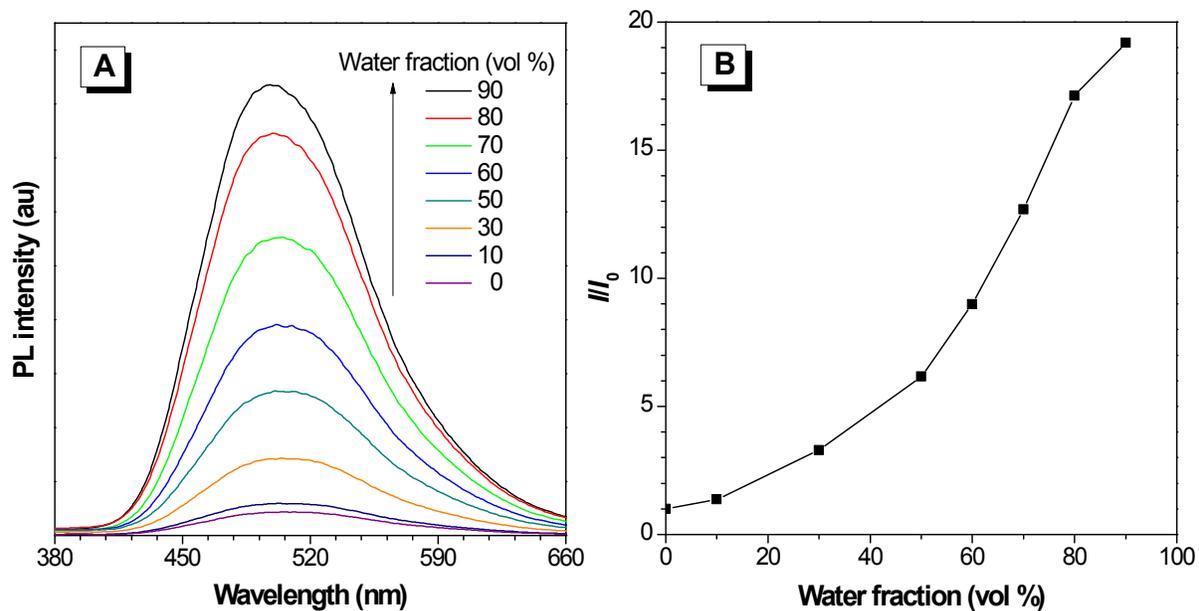
Fig. S2 IR spectra of (A) 1a, (B) 2a and (C) P1a2a.



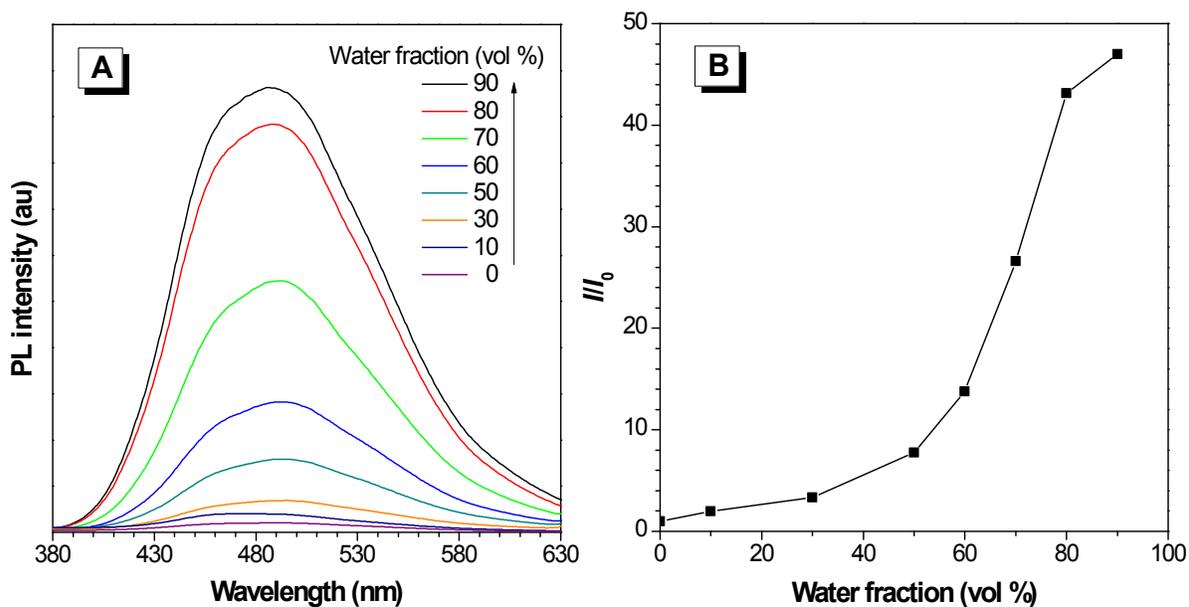
**Fig. S3** (A) PL spectra of P1a/2b in THF/water mixtures with different water fractions. (B) Plot of relative emission intensity ( $I/I_0$ ) versus the composition of the aqueous mixture of P1a/2b. Solution concentration: 10  $\mu$ M; excitation wavelength: 350 nm.



**Fig. S4** (A) PL spectra of P1a/2c in THF/water mixtures with different water fractions. (B) Plot of relative emission intensity ( $I/I_0$ ) versus the composition of the aqueous mixture of P1a/2c. Solution concentration: 10  $\mu$ M; excitation wavelength: 350 nm.



**Fig. S5** (A) PL spectra of P1a/2d in THF/water mixtures with different water fractions. (B) Plot of relative emission intensity ( $I/I_0$ ) versus the composition of the aqueous mixture of P1a/2d. Solution concentration: 10  $\mu$ M; excitation wavelength: 350 nm.



**Fig. S6** (A) PL spectra of P1a/2e in THF/water mixtures with different water fractions. (B) Plot of relative emission intensity ( $I/I_0$ ) versus the composition of the aqueous mixture of P1a/2e. Solution concentration: 10  $\mu$ M; excitation wavelength: 350 nm.