Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Amphiphilic gels of solvatochromic fluorescent poly(2-oxazoline)s containing D–π–A pyrenes

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A. General methodology

Instruments All ^{1}H NMR spectra were recorded on a JEOL LMN-EX400 instrument (^{1}H: 400 MHz) and Bruker DPX 300 instrument (^{1}H: 300 MHz) using tetramethylsilane (TMS) as the internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT-IR 469 Plus spectrometer. Thermogravimetric analyses (TGA) were carried out on a SII TG/DTA 6200 (SEIKO) under a dinitrogen atmosphere with a heating rate of 5 °C/min. All photophysical measurements in solution were carried out at room temperature (298 K), using dilute solutions with optical densities (O.D.) of ~0.1 at the maximum absorption wavelength in quartz cells (path length: 1 cm). All sample solutions were deaerated by bubbling with argon gas for 15 min before the measurements. UV-Vis spectra were recorded on a JASCO V-670 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. Maximum fluorescence wavelengths obtained from the fluorescence spectrometer were converted to wavenumbers using the equation $I(\nu) = \lambda^2 I(\lambda)$. Absolute quantum yields (Φ_{FL}) and the fluorescence spectra of amphiphilic gels were measured with a Hamamatsu Photonics Quantaurus QY, equipped with an integral sphere. The measurement error for the obtained Φ_{FL} values on this instrument is ±3%.

Materials. Unless otherwise noted, all reagents and chemicals were used without further purification. Diisopropylcarbodiimide (DIC), *n*-butyllithium, sodium *tert*-butoxide, hexamethylene diisocyanate (HDI), 1,8-diazabicycloundec-7-ene (DBU), and 2-methyl-2-oxazoline were obtained from TCI (Tokyo, Japan). Piperidine, $Pd(OAc)_2$, and diethylamine (DEA) were obtained from Wako Pure Chem. (Tokyo, Japan). Poly(2-ethyl-2-oxazoline) (M_w = 50,000 g/mol) was purchased from Sigma-Aldrich Japan 3 (Tokyo, Japan). Special grade dimethylacetamide (DMA) was purchased from Kanto Chem. (Tokyo, Japan). Spectrograde toluene, THF, dichloromethane (DCM), dimethylformamide (DMF), acetonitrile (MeCN), ethanol (EtOH), methanol (MeOH), and 4 Å molecular sieves were purchased from Nacalai Tasque (Kyoto, Japan). 4 Å molecular sieves were activated by heating under vacuum at 200 °C for 30 min. Commercially available DCM and DMF were dried by treatment with activated 4 Å molecular sieves, and the thus obtained solvents were subsequently stored under argon. MeCN was used after purification by distillation. 1-

Hydroxycarbonyl-6-(piperidin-1-yl)pyrene (**PCA**) was prepared according to a previously reported procedure.[1] The water used for photophysical measurements was purified using a Milli-Q® water purification system (Merck Millipore, USA).

Polymerization of 2-methyl-2-oxazoline (M_n = 13620 g/mol)[2]

A 100 mL two-neck flask was charged with a mixture of 2-methyl-2-oxazoline (15 g, 175 mmol), benzyl bromide (200 mg, 1.2 mmol) and MeCN (25 mL) and sealed under nitrogen, before being heated to 120 °C for 72 h. The resulting poly(*N*-acetylethylenimine) (**POZO**) was isolated by dissolving in MeOH and precipitation into diethyl ether, and dried *in vacuo* to give **POZO** (13.9 g) as a white solid in 93% yield.

Partial hydrolysis of POZO[2]

POZO was dissolved in an aqueous NaOH solution (Table S1), and the resulting mixture was heated to reflux for 12 h, before the water was removed under reduced pressure. The resulting random poly(ethylenimine/*N*-acetylethylenimine) copolymer (**POZO-NH**) was extracted with CH_2Cl_2 and dried *in vacuo*. The degree of hydrolysis was determined by ^{1}H NMR spectroscopy.

Table S1. Partial hydrolysis of **POZO**

Entry	**POZO** [g]	NaOH/NCOMe [%]	NaOH [mmol]	Water [mL]	Hydrolysis [%]	Yield [g]
POZO-NH-1	4	4	1.9	40	1.7	2.88 (72%)
POZO-NH-2	2	10	2.4	20	5.1	1.71 (85%)
POZO-NH-3	3	20	7.2	30	12	7.89 (79%)
POZO-NH-4	1	20	2.4	10	9.7	2.46 (82%)

Amidation of POZO-NH (POZO-py)

A suspension of **POZO-NH** (300 mg) in benzene (5 mL) was freeze-dried and dissolved in CH_2Cl_2 (3 mL). Then, a solution of **PCA** in CH_2Cl_2 (3 mL) and DMF (5 mL) was stirred under argon and cooled to 0 °C, before diisopropylcarbodiimide (140 mg, 0.88 mmol) was added. The mixture was stirred at room temperature for 30 minutes, before the **POZO-NH** solution was added. After the mixture had been stirred for 12 h, the resulting urea was removed by filtration, and the solvent was removed *in vacuo*. The obtained residue was purified with Sephadex LH-20, and the resulting polymer was precipitated from CH_2Cl_2 into hexane to give **POZO-py** as a pale yellow solid.

Table S2. Reaction conditions for the partial hydrolysis of **POZO-NH**.

Entry	Reactant	**PCA** equilibrium (**PCA**/NH-group)	Hydrolysis change [%]	Pyrene [%]	Yield [mg]
POZO-py-1	**POZO-NH-1**	10	1.70→0.77	0.82	214 (72 %)
POZO-py-2	**POZO-NH-2**	0.2	5.10→4.00	1.01	221 (74 %)
POZO-py-3	**POZO-NH-3**	0.2	12.0→10.3	1.27	222 (74 %)

Cross-Linking of POZO-py

A 50 mL flask was charged with **POZO-py** (300 mg), hexamethylene diisocyanate (HDI), DBU, and DMF (2 mL), and the resulting mixture was stirred at room temperature for a time under a nitrogen atmosphere. The reaction time and usage of HDI and DBU are listed in Table 2. The resulting (**POZO-py amphigel**) was isolated and purified by Soxhlet extraction with methanol, and dichloromethane consecutively.

Partial hydrolysis of PEtOZO.

PEtOZO (3.0 g) was dissolved in an aqueous NaOH solution (50 mL, 60 mmol) and the resulting mixture was heated to reflux for 12 h, before the water was removed under reduced pressure. The resulting random poly(ethylenimine/*N*-ethanoylethylenimine) copolymer (**PEtOZO-NH**) was extracted with CH_2Cl_2 and dried in a vacuum-dry oven, to afford 2.01 g (67%). The degree of hydrolysis (4.7%) was calculated by ^1H NMR spectroscopy.

Amidation of PEtOZO-NH (PEtOZO-py)

A suspension of **PEtOZO-NH** (500 mg) in benzene (5 mL) was freeze-dried and dissolved in CH_2Cl_2 (5 mL). Then, a solution of **PCA** (34 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) and DMF (10 mL) was stirred under argon and cooled to 0 °C, before diisopropylcarbodiimide (0.23 mL, 0.15 mmol) was added. The mixture was stirred at room temperature for 30 minutes, before the **PEtOZO-NH** solution was added. After the mixture had been stirred for 12 h, the resulting urea was removed by filtration. The solvent was removed *in vacuo*, and the residue was purified with Sephadex LH-20. The resulting polymer was precipitated from CH_2Cl_2 into hexane to afford

PEtOZO-py (351 mg, 70%) as a pale yellow solid. The degrees of hydrolysis (4.1%) and amidation (0.6%) were calculated by ^{1}H NMR spectroscopy.

Cross-Linking of PEtOZO-py

A 50 mL flask was charged with **PEtOZO-py** (1.0 g, including 0.12 mmol amine unit), hexamethylene diisocyanate (50 mg, 0.30 mmol), DBU (84 mg, 0.50 mmol), and DMF (3 mL) and stirred at room temperature for 1 h under an atmosphere of nitrogen. The resulting (**PEtOZO-py amphigel**) was purified and isolated by Soxhlet extraction with methanol and dichloromethane consecutively. to afford 0.86 g (85%).

B. ^{1}H NMR spectra

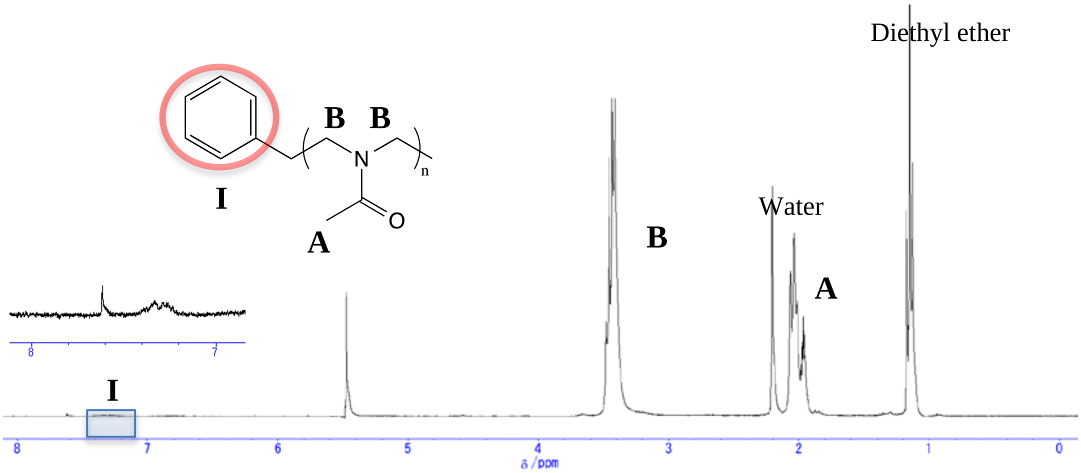


Fig. S1. ^{1}H NMR spectrum of **POZO** (M_n = 13620 g/mol) in CD_3CN at room temperature.

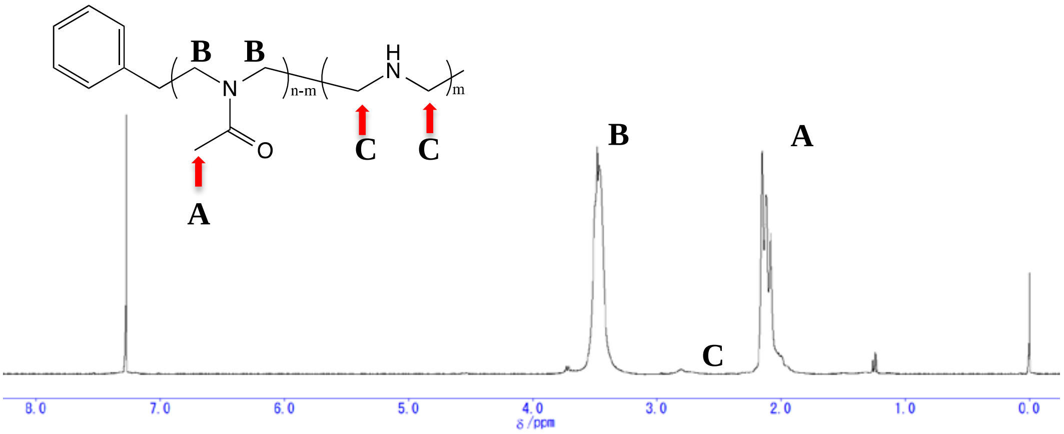


Fig. S2. ^{1}H NMR (400 MHz) spectrum of **POZO-NH-1** (hydrolysis: 1.7%) in $CDCl_3$ at room temperature.

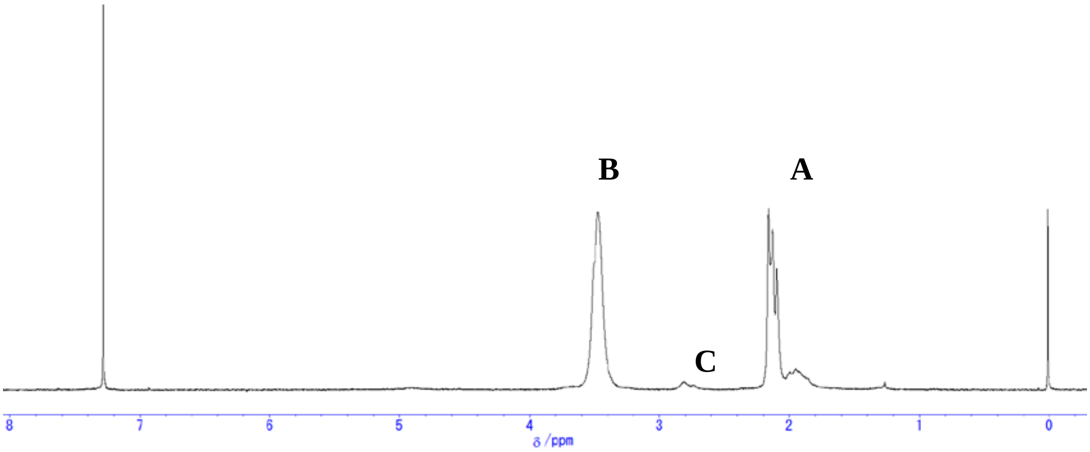


Fig. S3. ^{1}H NMR spectrum of **POZO-NH-2** (hydrolysis: 5.1%) in $CDCl_3$ at room temperature.

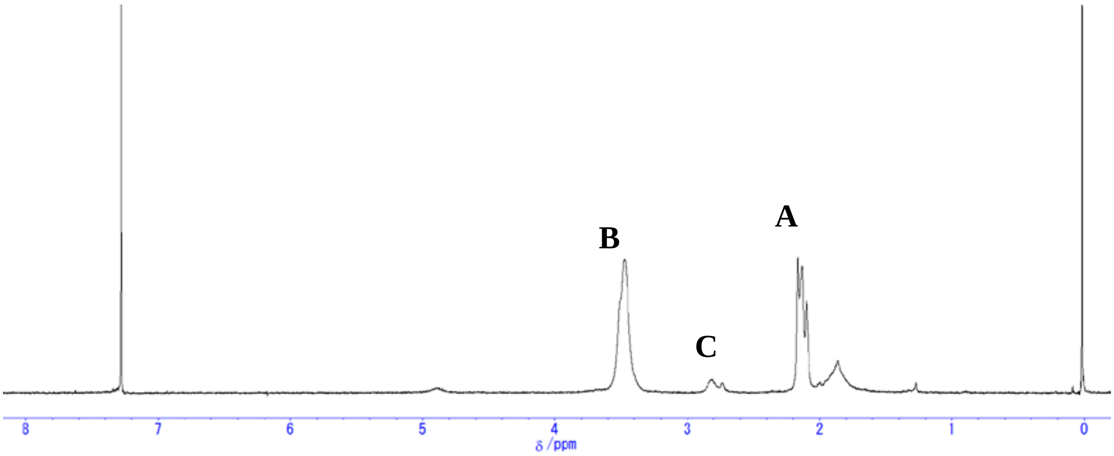


Fig. S4. ^{1}H NMR spectrum of **POZO-NH-3** (hydrolysis: 12.0 %) in $CDCl_3$ at room temperature.

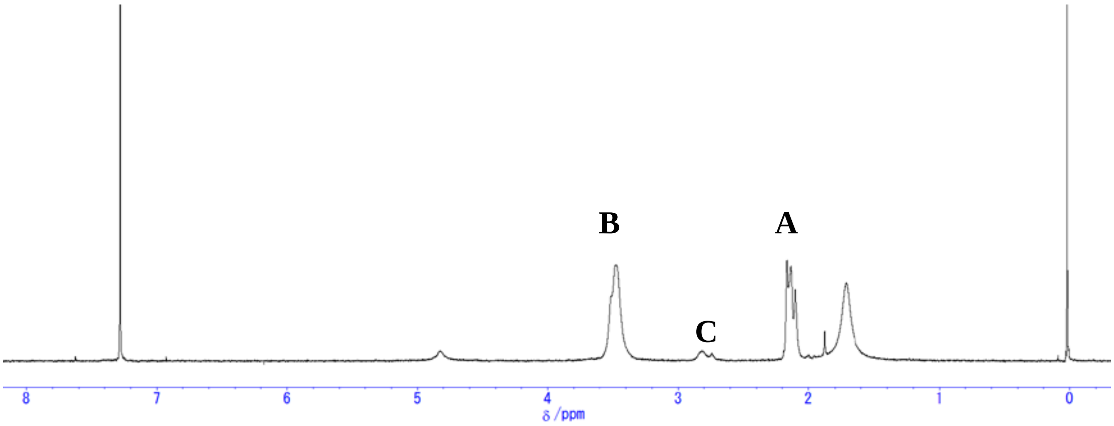


Fig. S5. ^{1}H NMR spectrum of **POZO-NH-4** (hydrolysis: 9.7%) in $CDCl_3$ at room temperature.

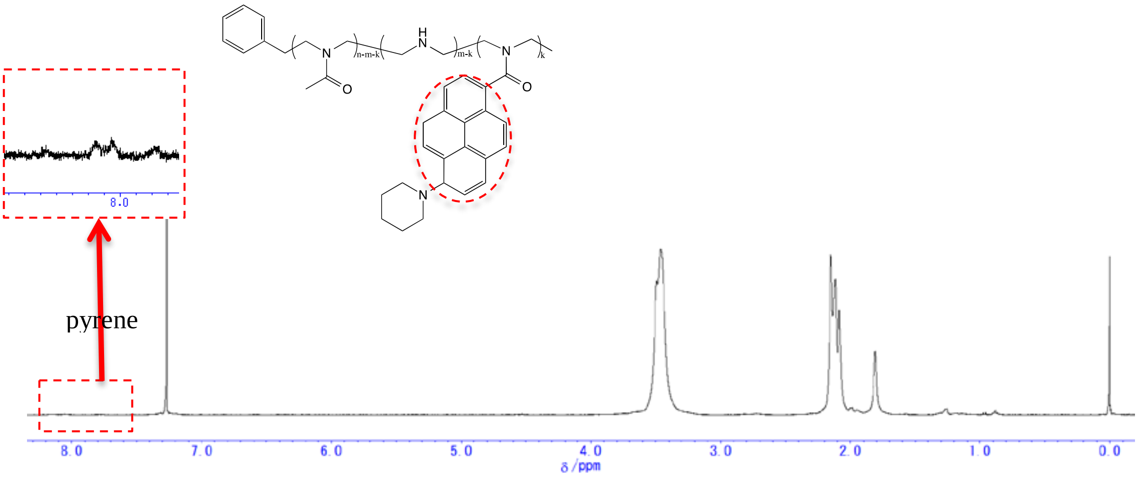


Fig. S6. ^{1}H NMR spectrum of **POZO-py-1** (hydrolysis: 0.77%; amidation: 0.82%) in $CDCl_3$ at room temperature.

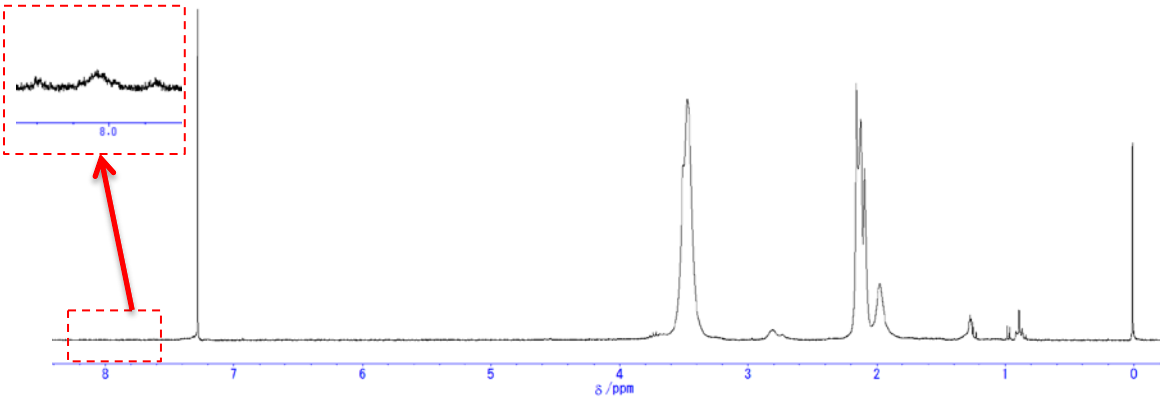


Fig. S7. ^{1}H NMR spectrum of **POZO-py-2** (hydrolysis: 4.0%; amidation: 1.01%) in CDCl$_3$ at room temperature.

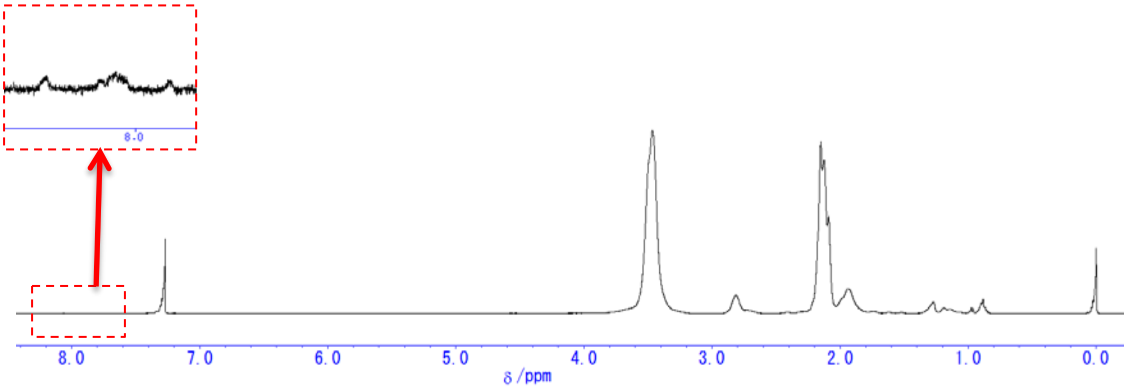


Fig. S8. ^{1}H NMR spectrum of **POZO-py-3** (hydrolysis: 10.3%; amidation: 1.27 %) in CDCl$_3$ at room temperature.

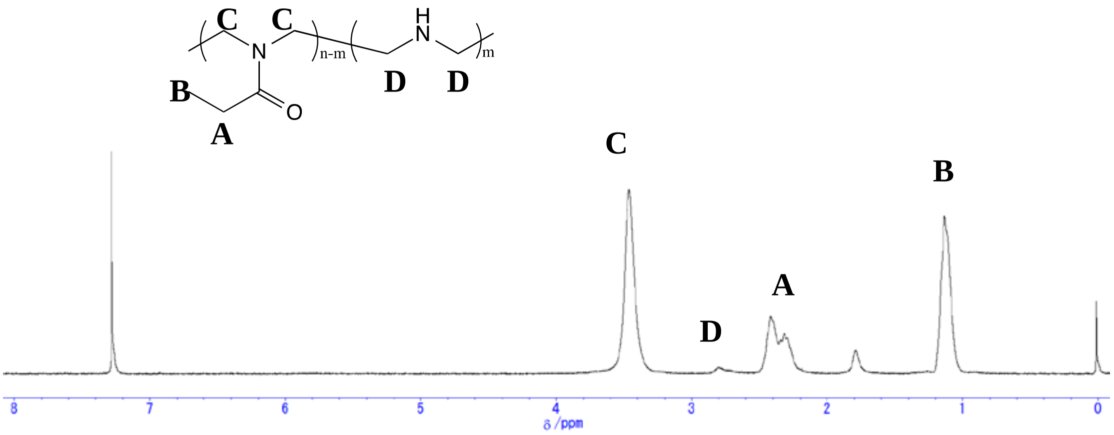


Fig. S9. ^{1}H NMR spectrum of **PEtOZO-NH** (hydrolysis: 4.7%) in CDCl$_3$ at room temperature.

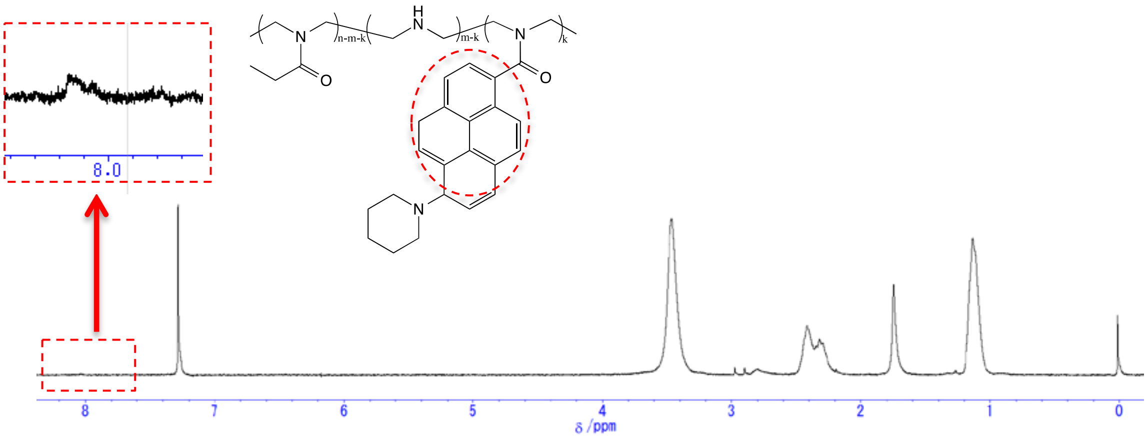


Fig. S10. ^{1}H NMR spectrum of **PEtOZO-py** (hydrolysis: 4.1%; amidation: 0.6%) in $CDCl_3$ at room temperature.

C. FT-IR spectra

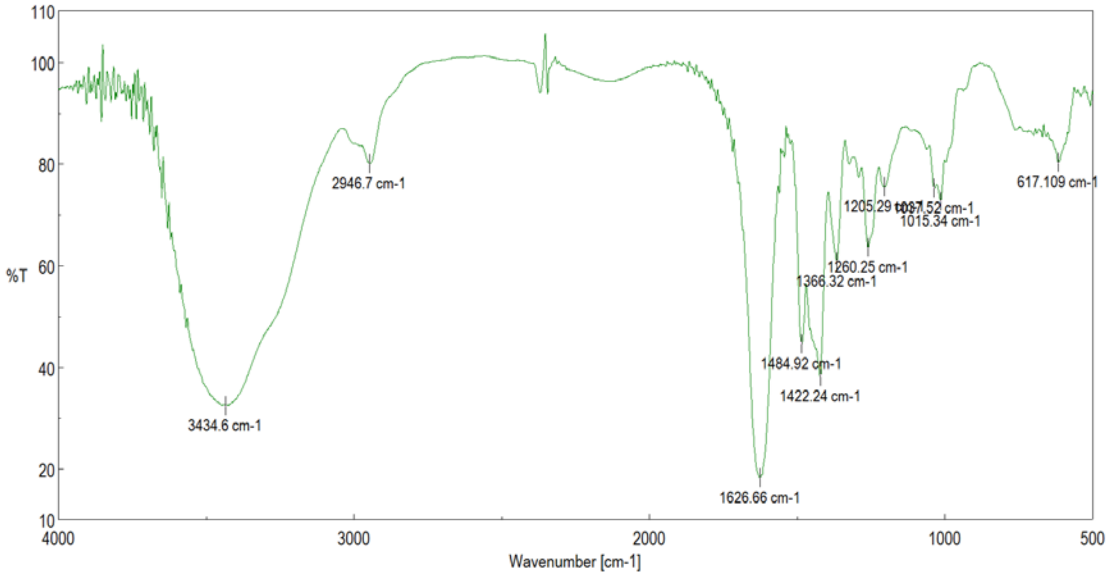


Fig. S11. FT-IR spectrum of **POZO-py-1** (hydrolysis: 0.77%; amidation: 0.82%).

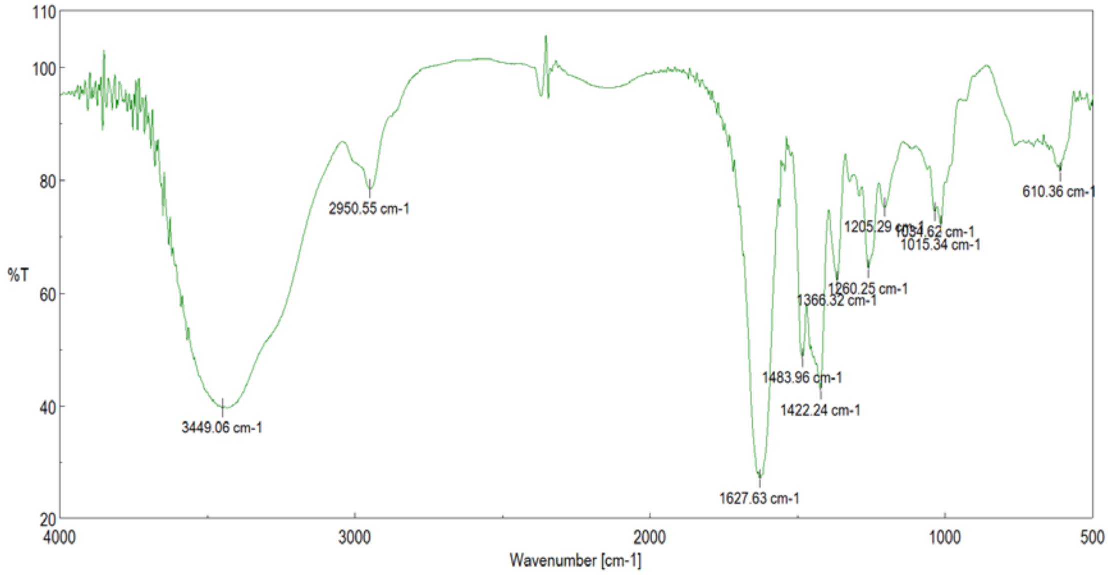


Fig. S12. FT-IR spectrum of **POZO-py-2** (hydrolysis: 4.0%; amidation: 1.01%).

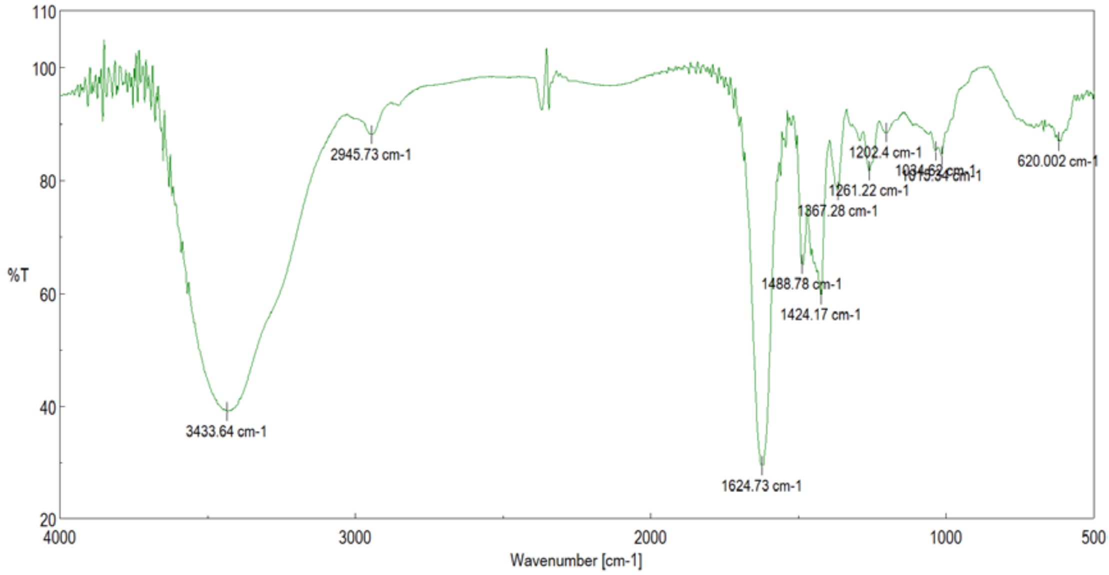


Fig. S13. FT-IR spectrum of **POZO-py-3** (hydrolysis: 10.3%; amidation: 1.27 %).

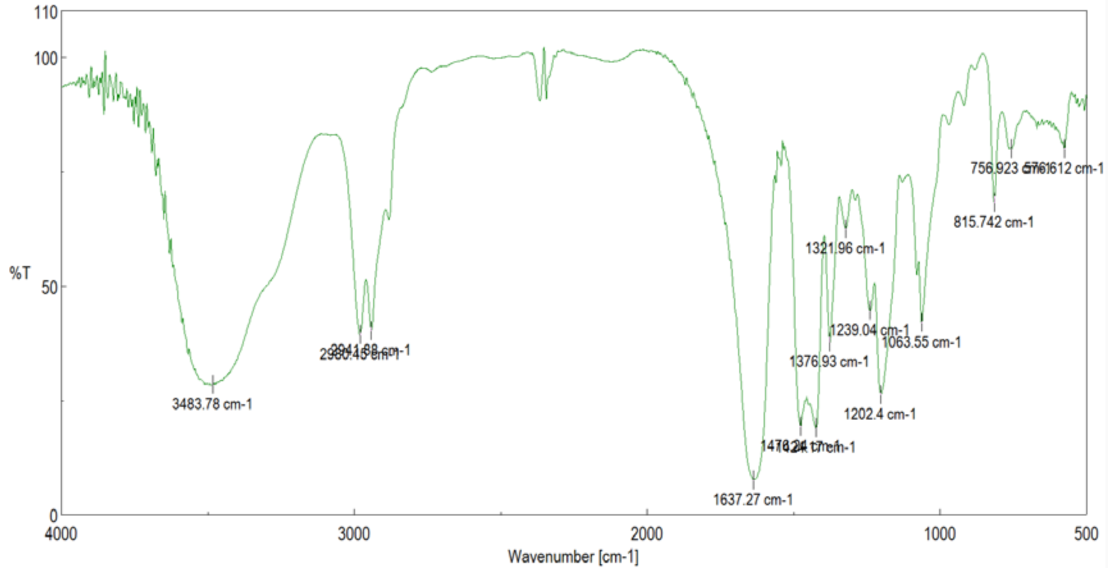


Fig. S14. FT-IR spectrum of **PEtOZO-py** (hydrolysis: 4.1%; amidation: 0.6%).

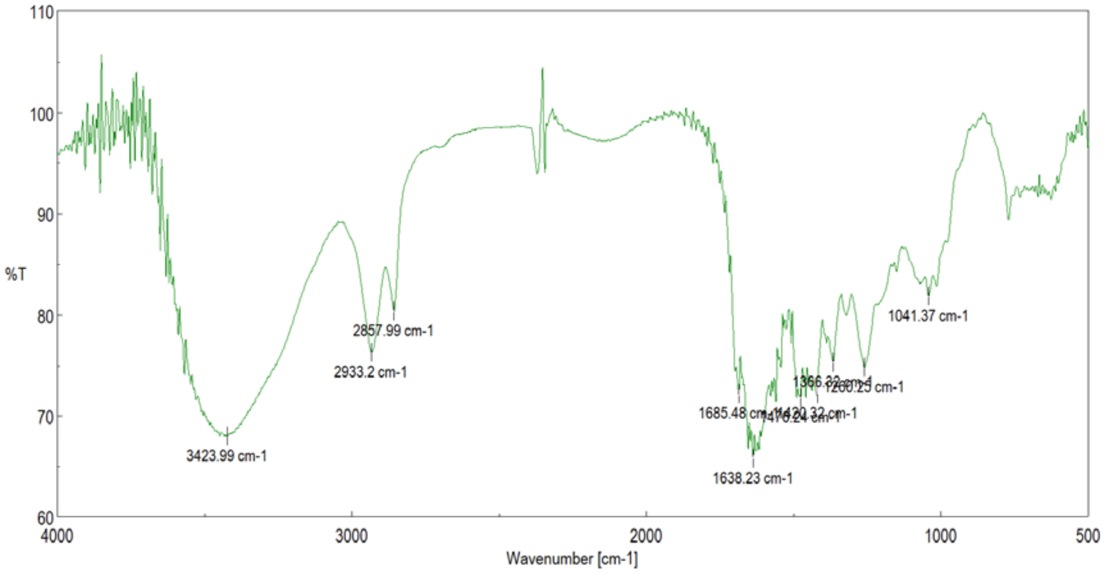


Fig. S15. FT-IR spectrum of **POZO-py-2 amphigel** (hydrolysis: 4.0%; amidation: 1.01%).

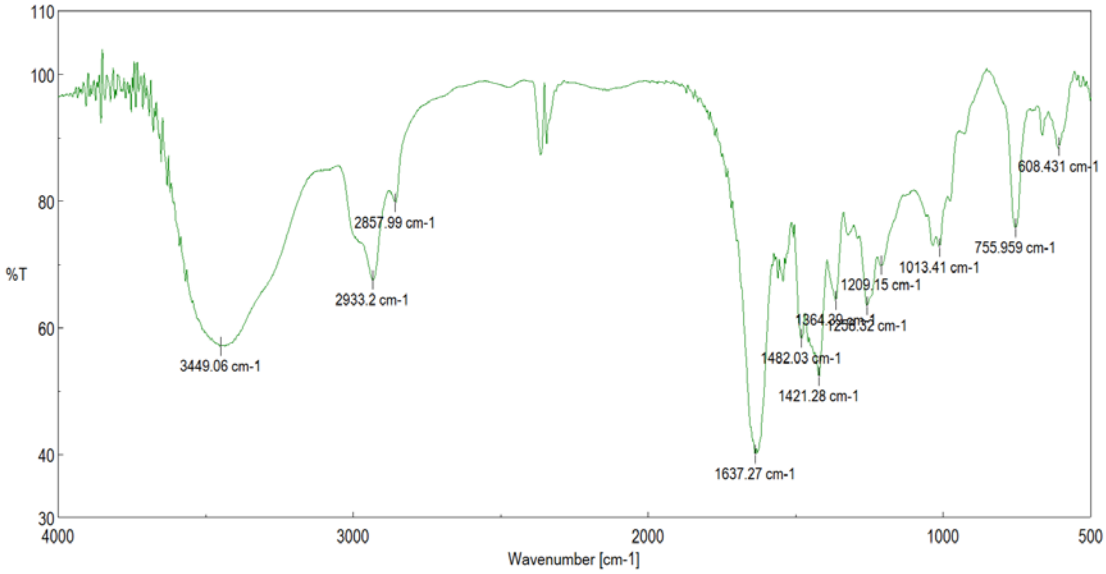


Fig. S16. FT-IR spectrum of **POZO-py-3 amphigel** (hydrolysis: 10.3%; amidation: 1.27 %).

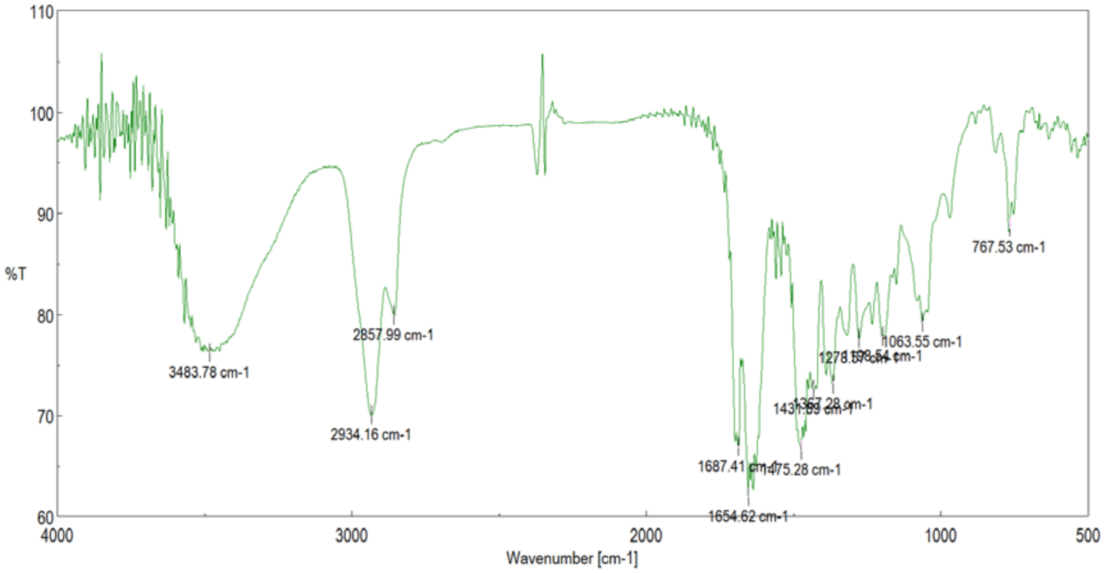


Fig. S17. FT-IR spectrum of **PEtOZO-py amphigel** (hydrolysis: 4.1%; amidation: 0.6 %).

C. Thermogravimetric analysis

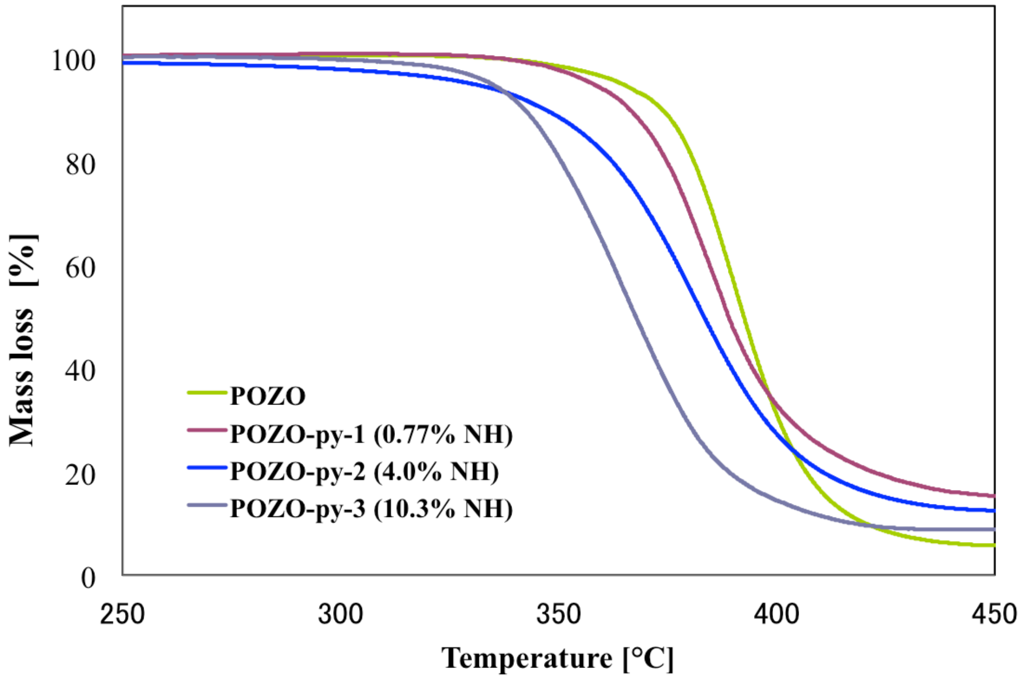
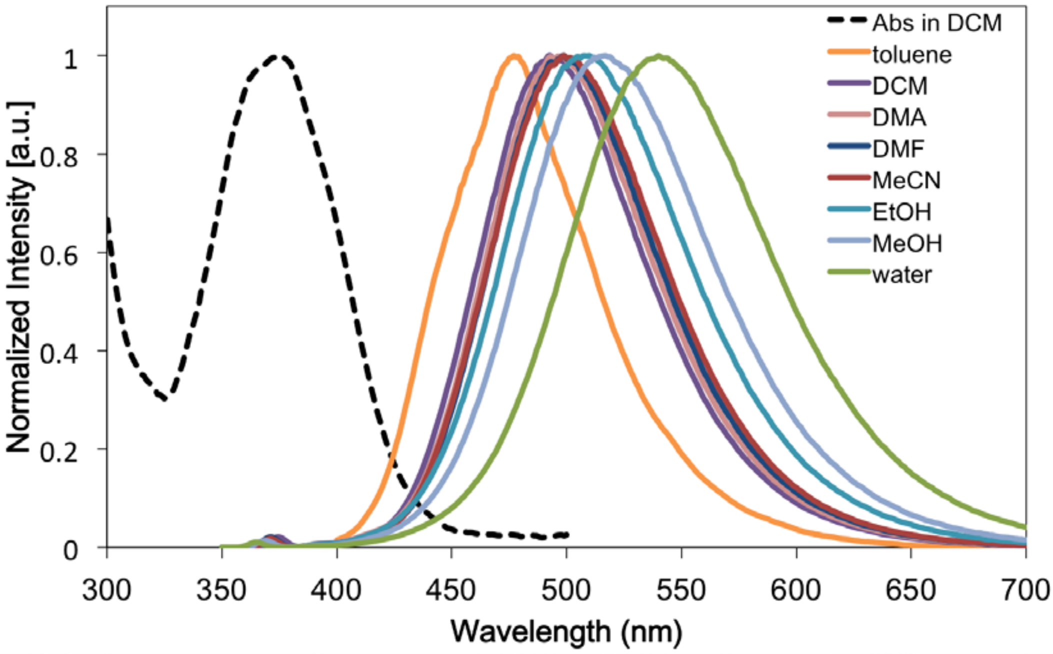


Fig. S18. TGA spectra of **POZO** and **POZO-py**.

D. Absorption and fluorescence spectra of POZO-py with different hydrolysis ratios

(a)



(b)

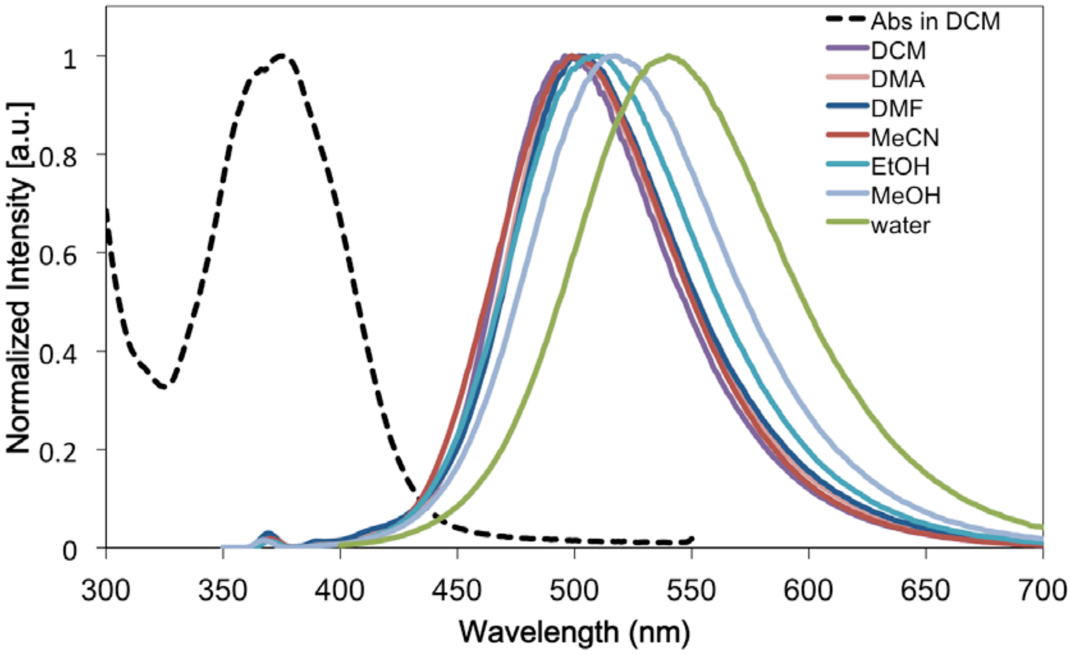


Fig. S19. UV-Vis absorption and fluorescence spectra of (a) **POZO-py-2** (4% NH) and (b) **POZO-py-3** (10.3% NH).

E. Quantum yields (Φ) of the model dye, PTA, in a mixed diethylamine/DCM solvent

In order to determine the effect of the ethylenimine and the dye moieties, we measured the analogous system using diethylamine (DEA) and the model dye, **PTA**. Upon changing the concentration of DEA, we did not observe a clear quenching arising from the hydrogen bonding of DEA in dilute solutions. When the concentration was <50%, the Φ of **PTA** was effectively quenched by DEA.

Table S3. Quantum yields (Φ) of **PTA** with different diethylamine ratios in DCM.

DEA/DCM [%]	λ_{em} [nm]	Φ [%]
0	456	89.9
0.5	460	91.5
1.0	460	91.4
2.0	460	89.8
5.0	463	87.5
10.0	464	88.2
50.0	455	53.2
100.0	435	41.1

F. Photophysical and swelling properties of PEtOZO-py amphigels

Table S4. Photophysical and swelling properties of **PEtOZO-py amphigel** (4.1% NH).

Entry	**PEtOZO-py amphigel**		
Solvent	$(W'-W)/W^a$	λ_{em} [nm]	Φ [%]
-	-	455	67
Toluene	0.8	451	80
DCM	21.3	456	76
DMA	10.1	474	81
DMF	7.9	471	80
MeCN	1.9	470	73
EtOH	8.3	471	80

MeOH	4.6	470	68
Water	3.4	469	70

[a] *W*: weight of the dried gel. *W*': weight of the swollen gel.

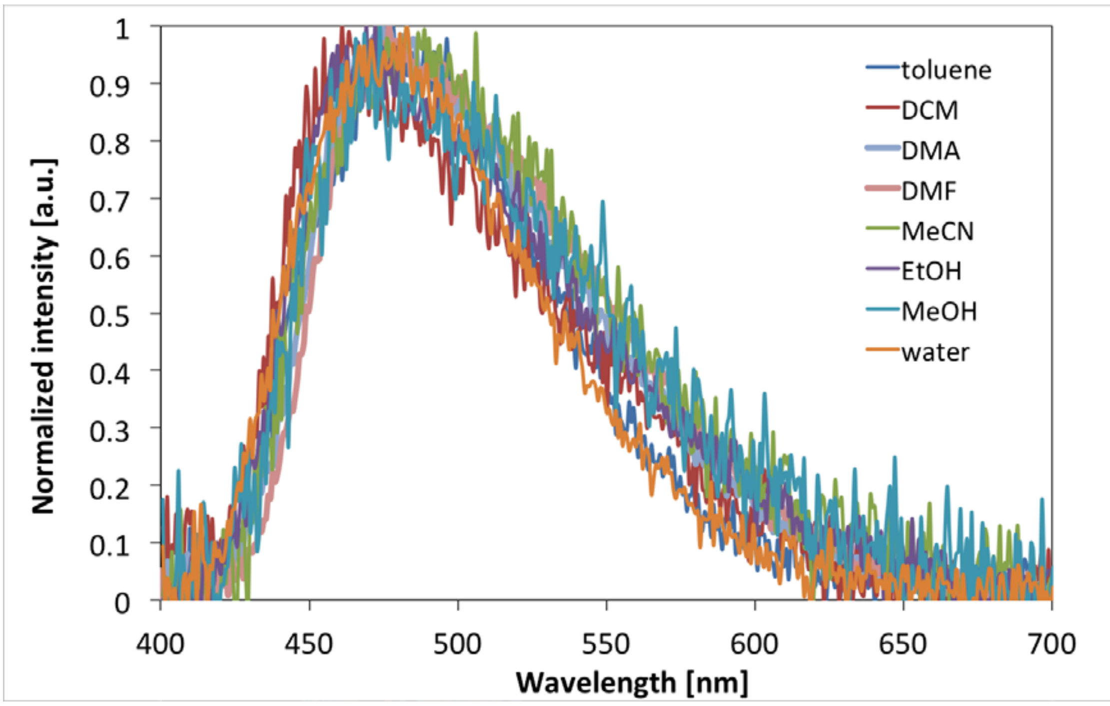


Fig. S20. Fluorescence spectra of **PEtOZO-py amphigel** in different solvents.

Reference

1 Y. Niko, Y. Cho, S. Kawauchi, and G. Konishi, *RSC Advances*, 2014, **4**, 36480-36484.

2 Y. Chujo, Y. Yoshifuji, K. Sada and T. Saegusa , *Macromolecules*, 1989, **22**, 1074-1077.