

Supporting Information

pH-Dependent morphology and photoresponse of azopyridine-terminated Poly(N-isopropylacrylamide) nanoparticles in water

*Hao Ren,^a Xing-Ping Qiu,^b Yan Shi,^c Peng Yang,^a Françoise M. Winnik^{*d,e}*

^a School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China.

^b Department of Chemistry, University of Montreal, CP 6128 Succursale Centre Ville, Montreal, QC, H3C 3J7, Canada.

^c School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

^d Laboratory of Polymer Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, Helsinki 00014, Finland

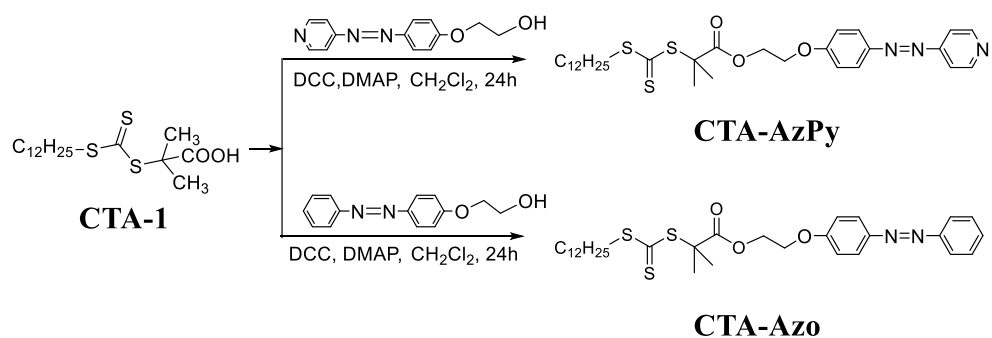
^e International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

E-mail: francoise.winnik@helsinki.fi

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1. Synthesis and characterization of CTA-Azo and CTA-AzPy



Scheme S1. Synthesis route of RAFT agent CTA-Azo and CTA-AzPy.

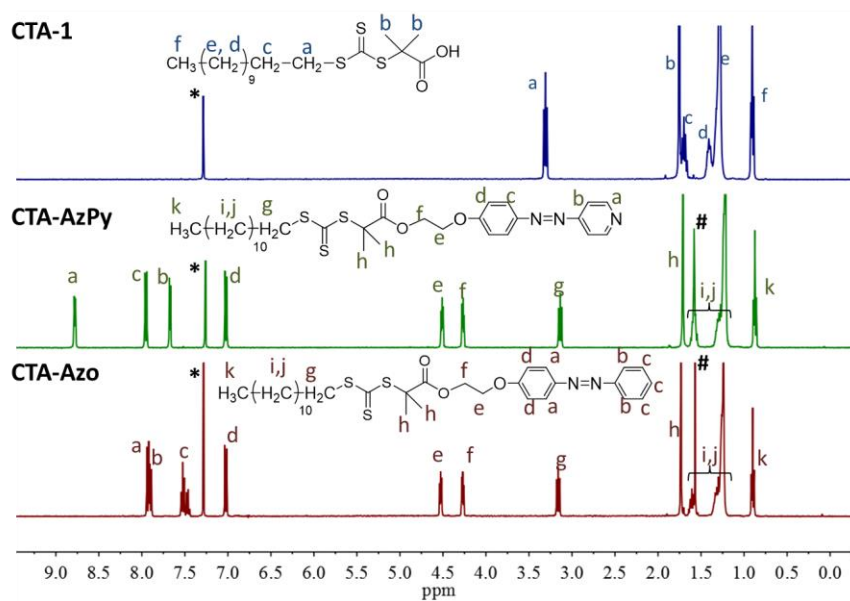


Figure S1. ^1H NMR spectrum of CTA-1, CTA-Azo and CTA-AzPy, solvent CDCl_3 . (* solvent peak, # H_2O peak)

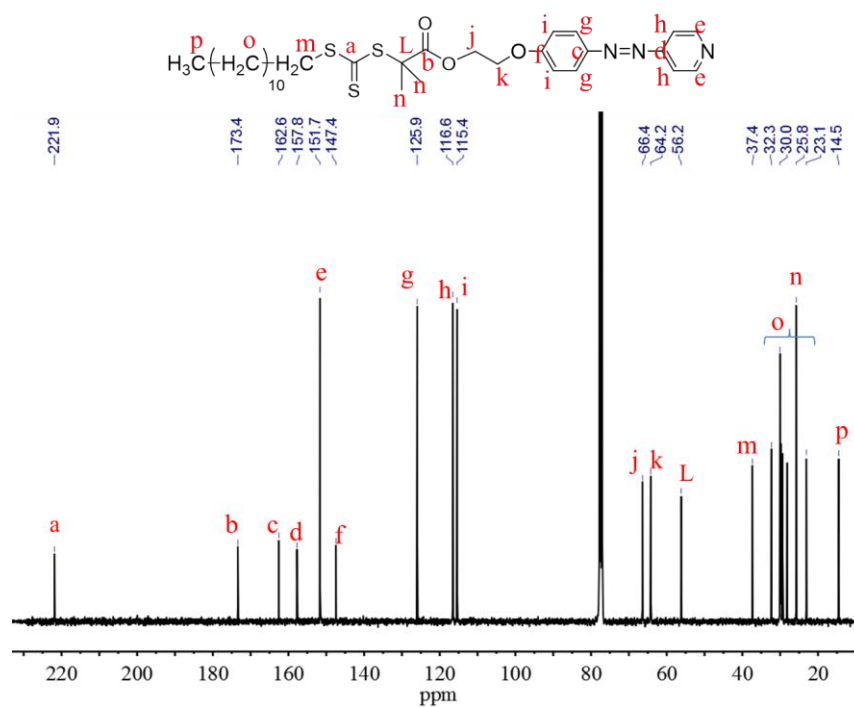


Figure S2. ^{13}C NMR spectrum of CTA-AzPy, solvent CDCl_3 .

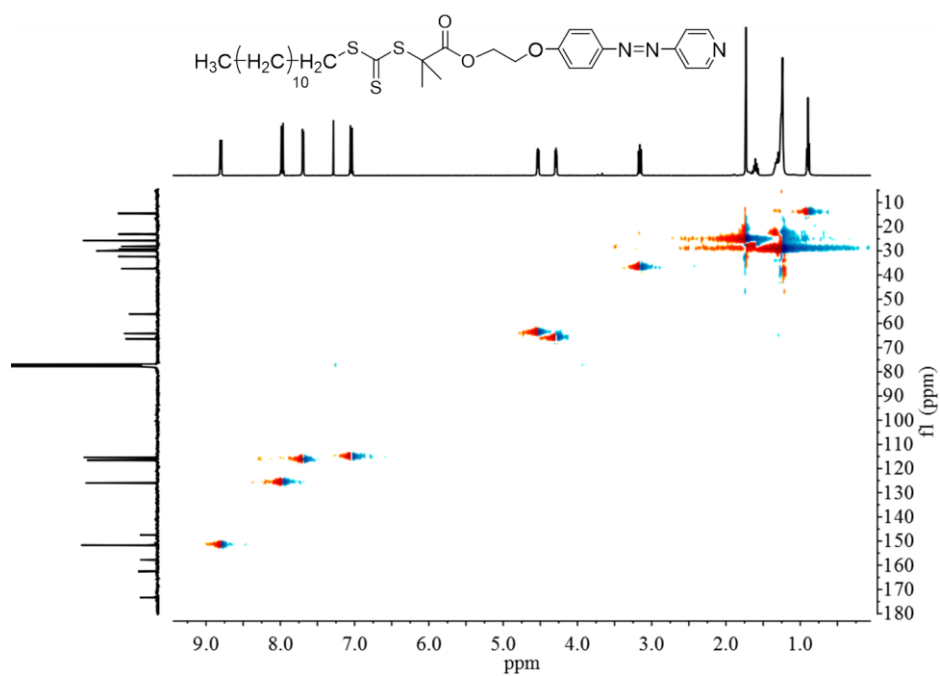
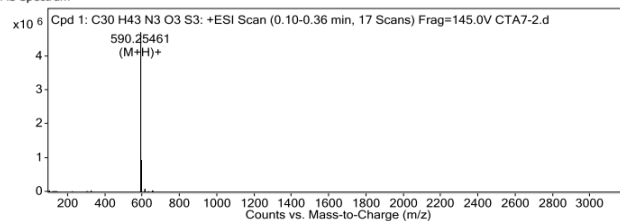


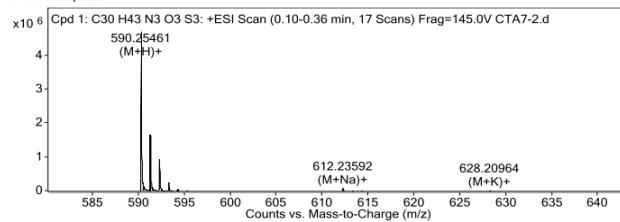
Figure S3. 2D-HMOC spectrum of CTA-AzPy, solvent CDCl_3 .

Data File	CTA7-2.d	Sample Name	CTA7-2
Sample Type	Sample	Position	P1-B2
Analysis Date	3/24/2017 4:48:34 PM	User Name	Marie-Christine
Acq Method	ESI_POS_DL.m	InstrumentName	TOF 6224
Comment			

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Ion Formula	Abund	Expe. m/z	Calc. m/z	Diff(ppm)
(M+H)+	C30H43N3O3S3	4696936.73	590.25461	590.25393	-1.14
(M+Na)+	C30H43N3O3S3	89783.27	612.23592	612.23588	-0.07
(M+K)+	C30H43N3O3S3	29057.59	628.20964	628.20981	0.27

Figure S4. MS spectrum of CTA-AzPy

2. Characterization of end functional PNIPAMs

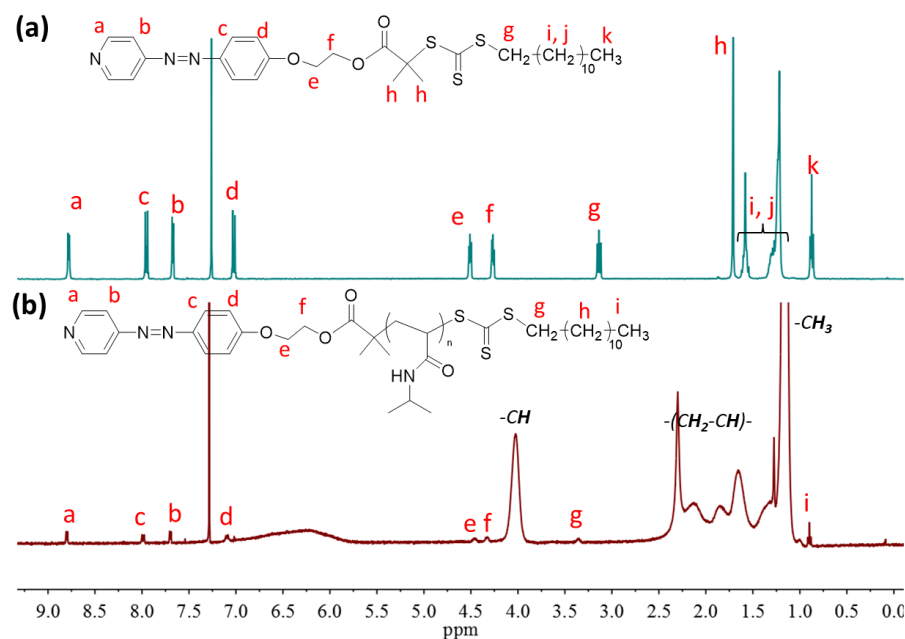


Figure S5. ^1H NMR spectrum and the peak assignment of (a), CTA-AzPy and C12-PN-AzPy 12K. (solvent CDCl_3)

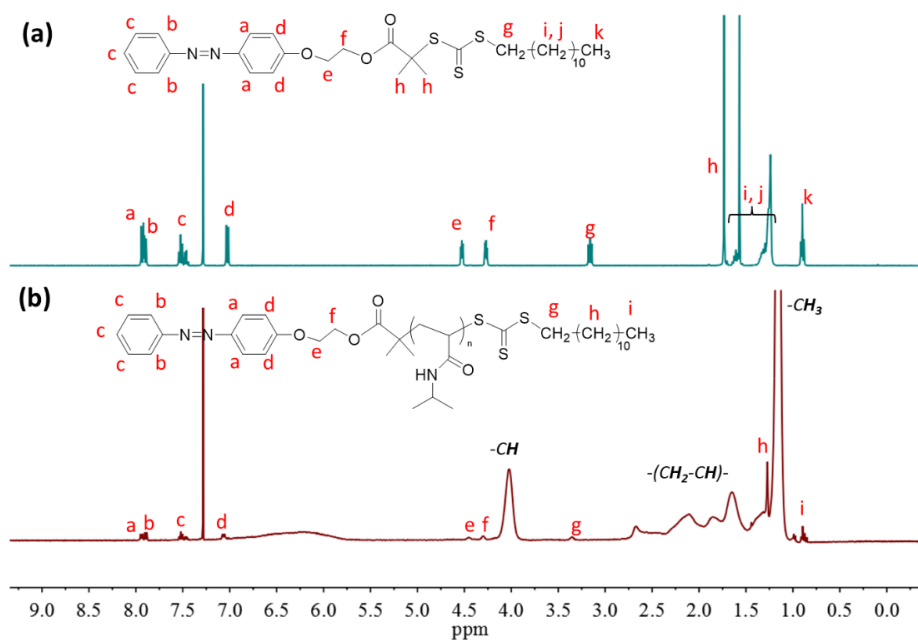


Figure S6 ^1H NMR spectrum and the peak assignment of (a), CTA-Azo and (b) C12-PN-Azo (solvent CDCl_3)

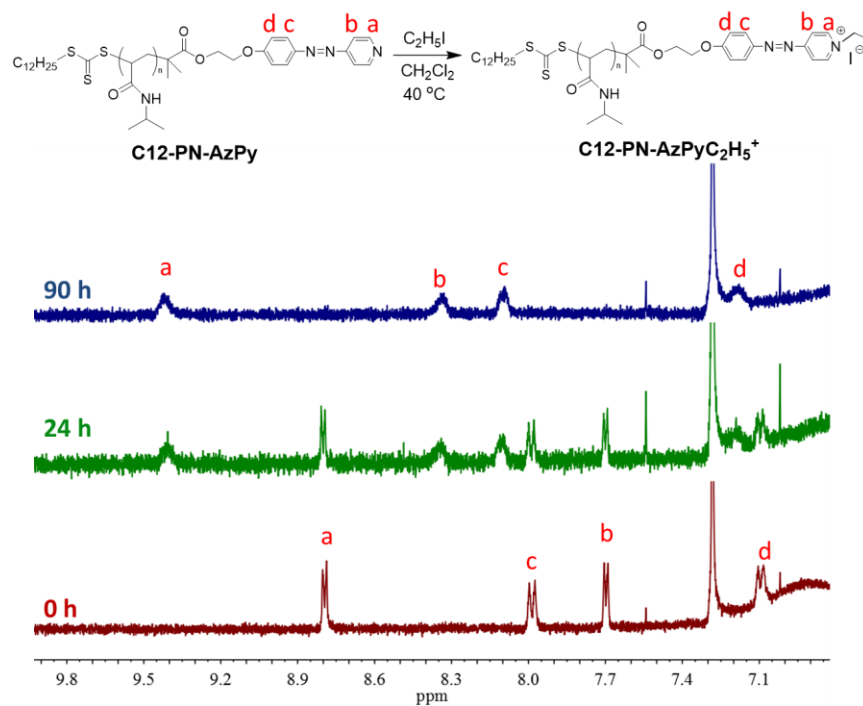


Figure S7 ^1H NMR spectrum and the peak assignment of C12-PN-AzPy 12K and C12-PN-AzPy C_2H_5^+ (solvent CDCl_3)

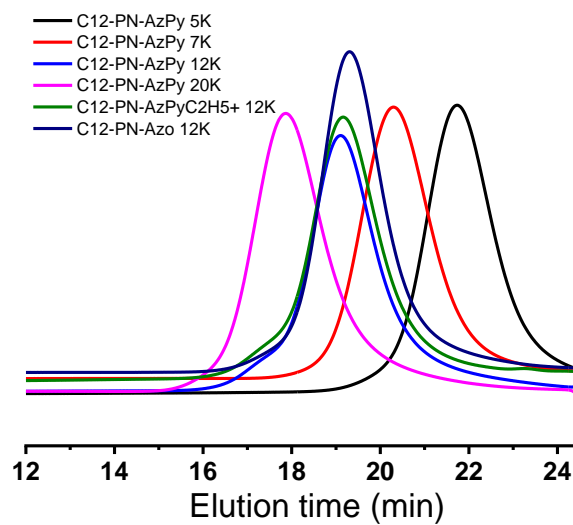


Figure S8. GPC analysis of C12-PN-AzPy, C12-PN-AzPy C_2H_5^+ and C12-PN-Azo. (DMF as eluent)

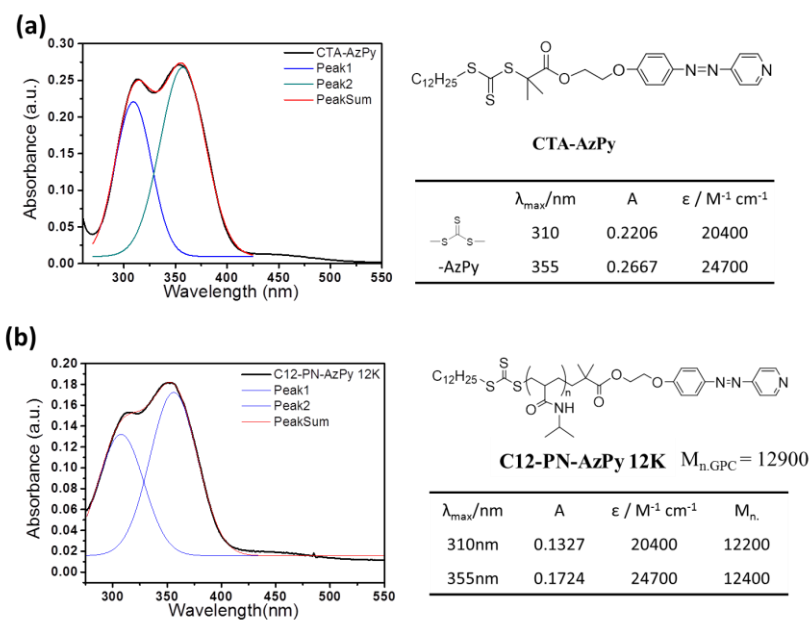


Figure S9. (a), UV-vis spectrum of CTA-AzPy and the determination of molar extinction coefficient (ϵ); (b), determination of molecular weight of C12-PN-AzPy 12K by UV-vis spectrum. (peak separation function, Gauss, fitting from 270nm to 450nm)

3. Characterization of self-assembly structure

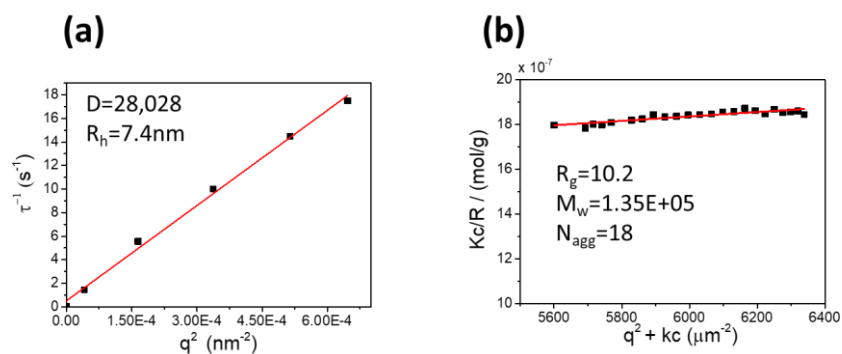


Figure S10. (a). Example of DLS plot and (b) Zimm plot of polymer micelles for C12-PN-AzPy 7K at 10 °C (k is constant for 5600 in this case.)

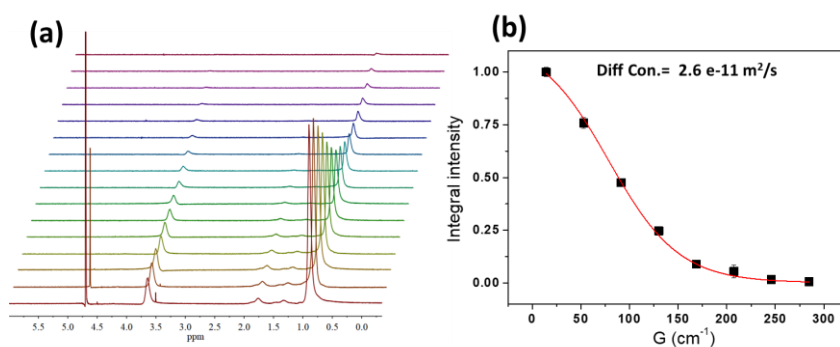


Figure S11. Diffusion NMR measurements of C12-PN-AzPy at 10 °C in D₂O. (a), Diffusion spectrum of C12-PN-AzPy 12K in D₂O.(b), Fitting curve of the diffusion constant (D) of C12-PN-AzPy 12K.

Table S1. Summary of the fitted diffusion constants and corresponding R_h values.

Sample name	M_n (g/mol)	D (m ² /s)	R_h (nm)
C12-PNIPAM-AzPy 5K	5800	3.5e-11	5.9
C12-PNIPAM-AzPy 7K	7800	2.6e-11	7.9
C12-PNIPAM-AzPy 12K	12900	2.6e-11	8.0
C12-PNIPAM-AzPy 20K	19700	1.9e-11	10.9
C12-PNIPAM-AzPyC ₂ H ₅ ⁺ 12K	12900	2.4e-11	8.62

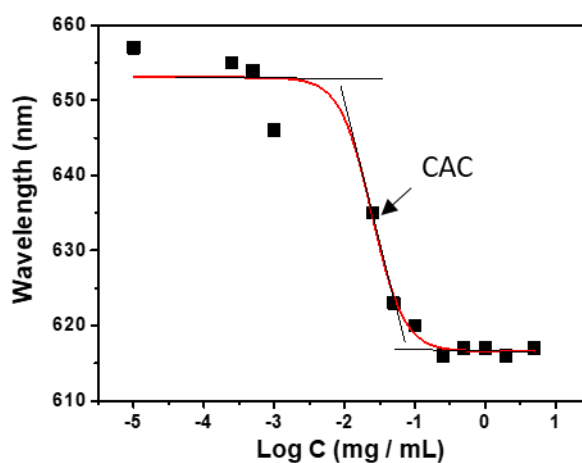


Figure S12. The plot of the maximum wavelength of the NR emission versus the C12-PN-AzPy 12K concentration.

4. Hydrolysis test

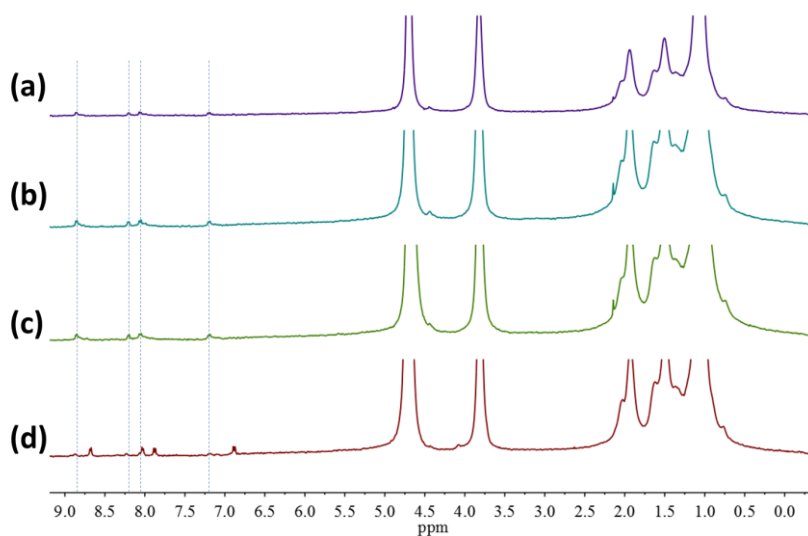


Figure. S13. Hydrolysis testing of C12-PN-AzPy 12K under acid condition (a), pH=3 after 25 hours; (b), pH=3 after 5 days; (c) pH=3 after 5 days and 24 hours under 70 °C; (d), pH=1 after 5 days. (Signal of ionized azopyridine at aromatic part shift to high field when hydrolysis occurs)

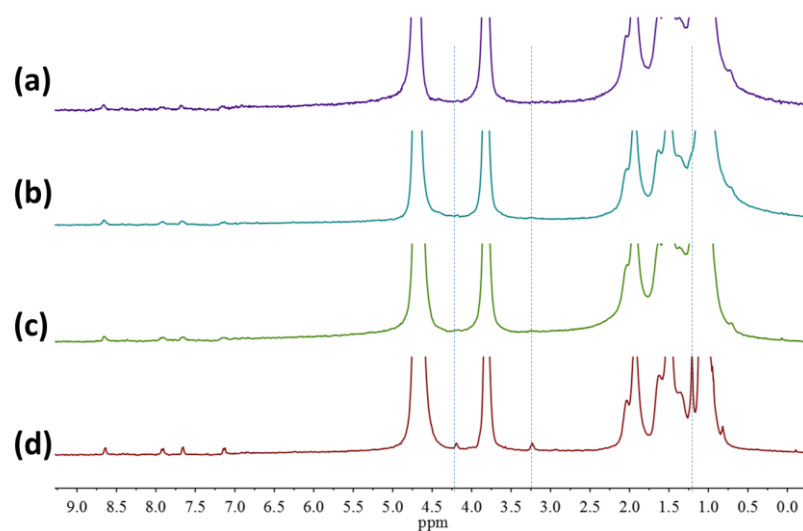


Figure. S14. Hydrolysis testing of C12-PN-AzPy 12K under base condition (a), pH=10 after 25 hours; (b), pH=10 after 5 days and 1.5 hours under 70 °C ; (c) pH=10 after 5 days and 24 hours under 70 °C; (d), pH=14 after 5 days 24 hours and under 70 °C. (Signal of azopyridine at aromatic part, CH₂ groups on C12 and HO-C2-AzPy becomes sharper when hydrolysis occurs)

5. UV-responsive properties.

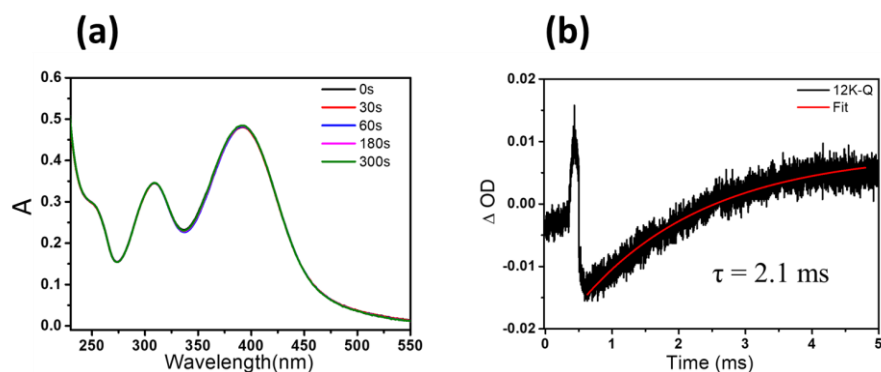


Figure S15. (a) UV-Vis spectra under different irradiation time (365 nm) and (b) Transient absorption spectra of C12-PN-AzPyC₂H₅⁺ 12K aqueous solution (0.5 mg/mL).

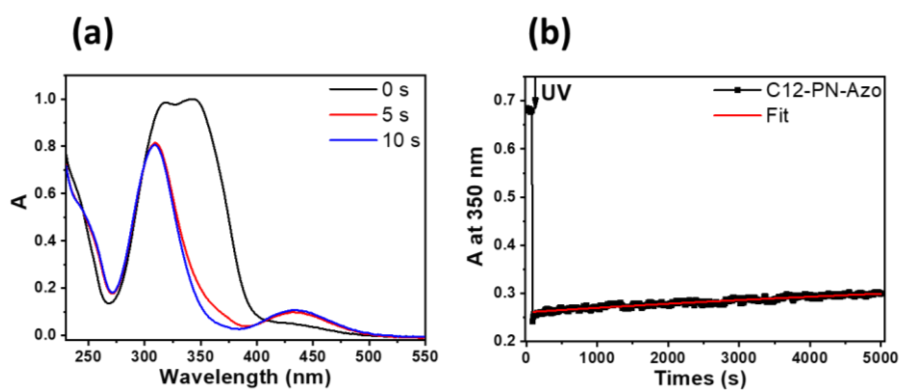


Figure S16. (a) UV-Vis spectra under different irradiation time (365 nm) and (b) Transient absorption spectra of C12-PN-Azo 12K aqueous solution (0.5 mg/mL, 10 °C).