

Supporting Information

Acid-Induced “Turn-On” Fluorescence of β -Aminoacrylate-based Molecule and Polymers Toward Anti-Counterfeiting Applications

*Xu Chen,^{†a,c} Bo Song,^{†a} Gaohuai Mei,^a Anjun Qin,^{*a} Ben Zhong Tang^{*b}*

^a State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, South China University of Technology, Guangzhou 510640, China.

^b Guangdong Basic Research Center of Excellence for Aggregate Science, School of Science and Engineering, The Chinese University of Hong Kong (Shenzhen), Longgang, Shenzhen, Guangdong 518172, China.

^c Institute for Engineering Medicine, Kunming Medical University, Kunming, 650500, China.

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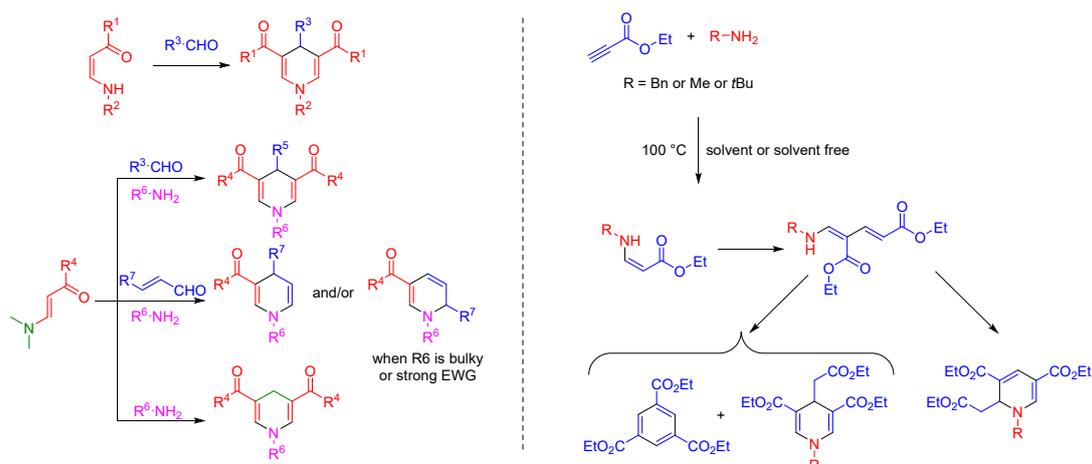
Materials and Instruments

All manipulations were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen.

Monomers oxybis(4,1-phenylene)dipropiolate (**M1**)¹, 1,1'-(oxybis(4,1-phenylene))-bis(prop-2-yn-1-one) (**M2**), and hexane-1,6-diylidipropiolate (**M3**)² were prepared according to literature procedures. Monomers 1,5-diaminopentane (**M4**), *N,N*-Diethylethylenediamine (**M5**), was purchased from TCI (Shanghai, China) Co. Ltd. Methyl propiolate and *n*-propylamine were purchased from Energy Chemical Co. Ltd. Titanium tetrachloride and acetic acid were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Concentrated sulfuric acid and concentrated nitric acid were purchased from Guangzhou Chemical Reagent Co. Ltd. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen before use. All other chemicals and reagents were purchased from commercial sources and used as received without further purification.

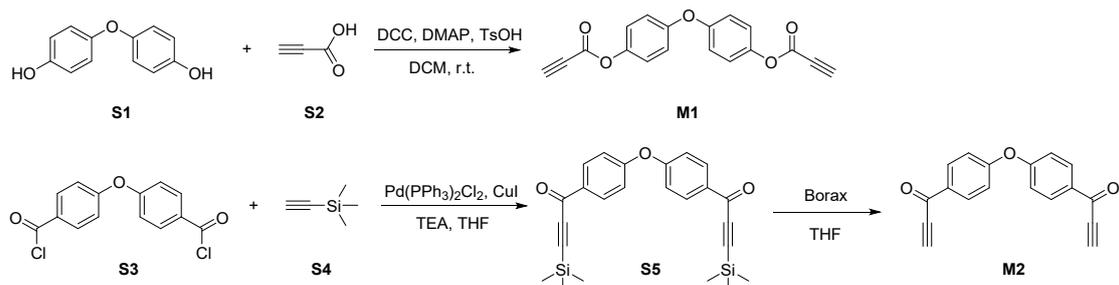
¹H and ¹³C NMR spectra were measured on a Bruker AVANCE 400 (400 MHz) or AVANCE DRX 500 (500 MHz) NMR spectrometer (Bruker, Germany) using deuterated chloroform (CDCl₃) or deuterated dimethyl sulfoxide (DMSO-*d*₆) as solvent and tetramethyl silane (TMS, $\delta = 0$) as internal reference. The weight-average molecular weights (M_w) and dispersity ($D = M_w/M_n$) of the polymers were measured by Waters 1515 gel permeation chromatography (GPC, Waters Associates, USA) system equipped with a RI detector. DMF containing 0.05 M LiBr was used as the eluent at a flow rate of 1.0 mL min⁻¹. A set of linear polymethyl methacrylate (PMMA) standards covering the M_w range of 10³~10⁷ were utilized for M_w and D calibration. Fourier transform infrared (FT-IR) spectra were measured on a Bruker Vector 33 FT-IR (Germany) spectrometer (KBr disk). Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer (USA). UV-vis absorption spectra were recorded on a SHIMADZU UV-2600 (Japan) spectrophotometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF mass) was performed using a Waters SYNAPT G2 HDMS mass spectrometry system (USA). Fluorescence quantum yields (QY) were measured with a Quantaaurus-QY C11347-11 absolute quantum yield spectrometer from Hamamatsu Photonics (Japan).

Cyclizations of β -Aminoacrylate/Enaminones toward Dihydropyridines



Scheme S1. Reported cyclizations of β -aminoacrylate/enaminones for dihydropyridine derivatives.³

Preparation of Monomers



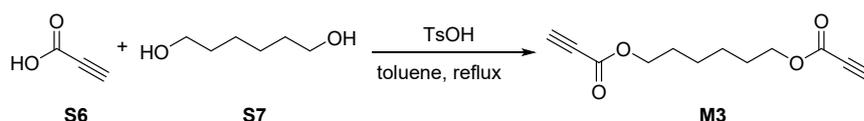
Scheme S2. Synthetic routes for monomers **M1** and **M2**.

Monomers **M1** and **M2** were prepared according to procedures reported by our group (Scheme S2).¹

White solid of **M1** was obtained in 75% yield. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.13 (d, J = 9.1 Hz, 4H), 7.03 (d, J = 9.1 Hz, 4H), 3.08 (s, 2H). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 155.11, 151.05, 145.36, 122.59, 119.73, 74.17. FT-IR (KBr disk), ν (cm⁻¹): 3416, 3273, 3240, 3072, 2127, 1715, 1591, 1494, 1209, 1175, 1092, 1011, 915, 843, 750, 699, 677, 614, 582, 516.

M2 (47 mg) as a white powder was obtained in 86% yield after purified by a silica gel column chromatography using petroleum ether/ethyl acetate (10:1 v/v) as eluent. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 8.21 (d, 4H), 7.14 (d, 4H), 3.44 (s, 2H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 175.81, 161.12, 132.35, 132.25, 118.98, 80.48, 80.13. FT-IR (KBr disk), ν (cm⁻¹): 3195, 2090, 1639, 1585, 1497, 1312, 1243, 1162, 1004, 766.

Monomer **M3** was prepared according to the procedures in reference (Scheme S3).²

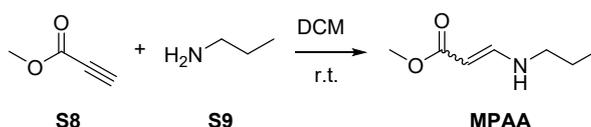


Scheme S3. Synthetic route for monomer **M3**.

To a 250 mL two-necked flask, 2.363 g (20 mmol) of compound **S7** and 100 mL of toluene were added, followed by 3.72 mL (60 mmol) of propiolic acid (**S6**). The reaction mixture was refluxed for 36 h using a condenser equipped with a Dean-Stark trap. After cooling the reaction mixture to room temperature, the toluene was removed by evaporation. The crude product was purified by column chromatography on silica gel, using a petroleum ether/ethyl acetate ($v/v = 10:1$) mixture as the eluent. Upon removal of most of the solvent, the solution was allowed to stand, resulting in the precipitation of colorless plate-like crystals of compound **M3**. The yield was 95%. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 4.20 (t, $J = 6.6$ Hz, 4H), 2.88 (s, 2H), 1.76 – 1.62 (m, 4H), 1.51 – 1.34 (m, 4H). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 152.78, 74.74, 74.55, 66.16, 28.18, 25.42. FT-IR (KBr disk), ν (cm⁻¹): 3228, 2945, 2868, 2113, 1699, 1477, 1252, 1078, 967, 905, 774, 713, 603, 423.

Preparation and Reaction of MPAA

The methyl-3-(propylamino)acrylate (MPAA) was prepared according to the click reaction methods reported in the literature (Scheme S4):¹



Scheme S4. Synthetic route to model compound MPAA.

In a 50 mL single-neck flask, 890 μ L of methyl propiolate (**S8**) (840.7 mg, 10 mmol) and 10 mL of dichloromethane (DCM) were added, followed by 904 μ L of n-propylamine (**S9**) (650.2 mg, 11 mmol). The mixture was stirred at room temperature for 2 h. Afterward, the solvent and excess *n*-propylamine were removed using a rotary evaporator, resulting in a colorless liquid compound MPAA. No further purification was necessary, and the yield was 99%. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.51 (m, *E*, 0.6H), 6.63 (m, *Z*, 0.4H), 4.73 (d, $J = 13.2$ Hz, *E*, 0.6H), 4.46 (d, $J = 8.0$ Hz, *Z*, 0.4H), 3.65 (d, 3H), 3.13 (m, *Z*, 0.8H), 3.01 (m, *E*, 1.2H), 1.58 (m, *Z*, 2H), 0.94

(m, *E*, 3H). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 171.26, 170.06, 152.52, 85.32, 80.98, 50.52, 50.45, 50.11, 24.50, 11.34, 11.06. FT-IR (KBr disk), ν (cm⁻¹): 3337, 2963, 2875, 1674, 1615, 1530, 1438, 1373, 1312, 1246, 1193, 1153, 1055, 989, 791, 663.

Compound DHPy can be prepared from compound MPAA under the catalysis of either TiCl₄,⁴ or concentrated H₂SO₄ as below:

TiCl₄ Catalyzed method: In a 100 mL two-neck flask, 429 mg of compound MPAA (3 mmol) was added, then 30 mL of anhydrous DCM was added under nitrogen to dissolve the compound. Under an ice bath, 66 μL of titanium tetrachloride was slowly dropped into the solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then poured into ice water and extracted with DCM. After removing solvent from the organic phase, the product was purified by silica gel column chromatography using a petroleum ether/ethyl acetate (v/v = 10:1) eluent, obtaining a pale-yellow oil with a 27.3% yield.

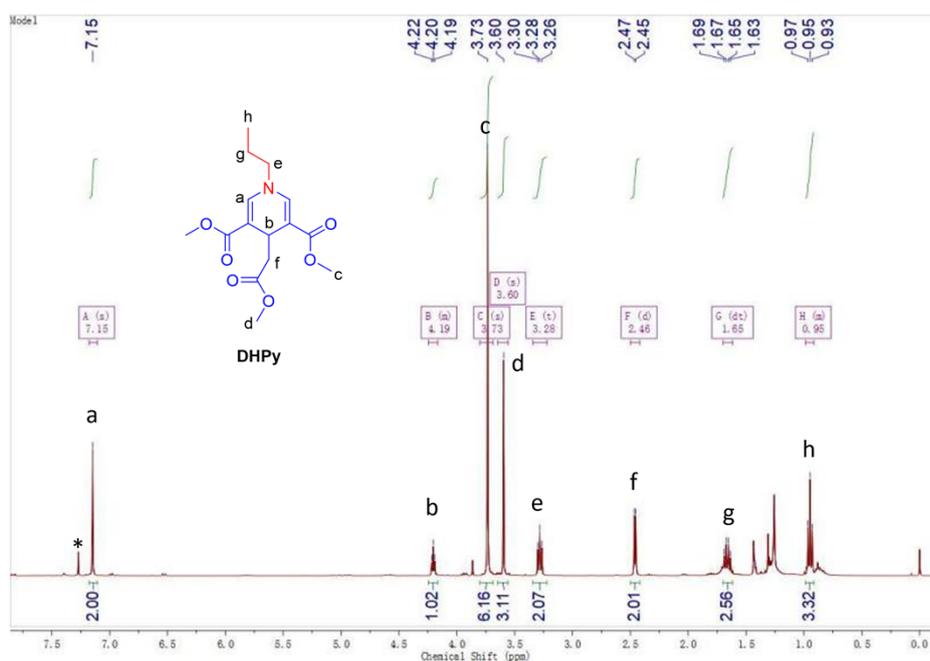


Fig. S1. ¹H NMR spectrum of compound DHPy in CDCl₃.

¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.15 (s, 2H), 4.25 – 4.17 (t, 1H), 3.73 (s, 6H), 3.60 (s, 3H), 3.28 (t, *J* = 7.1 Hz, 2H), 2.46 (d, *J* = 5.2 Hz, 2H), 1.65 (m, 2H), 0.99 – 0.91 (m, 3H). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 172.01, 167.32, 139.57, 105.51, 56.64, 51.40, 40.96, 29.49, 23.54, 10.80. FT-IR (KBr disk), ν (cm⁻¹): 2952, 2877, 1738, 1706, 1614, 1579, 1435, 1411, 1321, 1252, 1207, 1177, 1120, 1079, 1001, 918, 763.

Concentrated H₂SO₄ Catalyzed method: To a 50 mL single-neck flask, 429 mg of compound MPAA (3 mmol) was added. Concentrated sulfuric acid (183 μ L) was then slowly dropped into the flask with the mixture stirred. After reacting for 5 min, 20 mL of water was added to dilute the solution. The pH of the aqueous solution was adjusted to neutral using a 10% sodium carbonate solution. The organic phase was extracted with DCM, and the solvent was removed. The resulting product was purified by silica gel column chromatography using a petroleum ether/ethyl acetate ($v/v = 10:1$) eluent. A pale-yellow oil was obtained with a 68% yield.

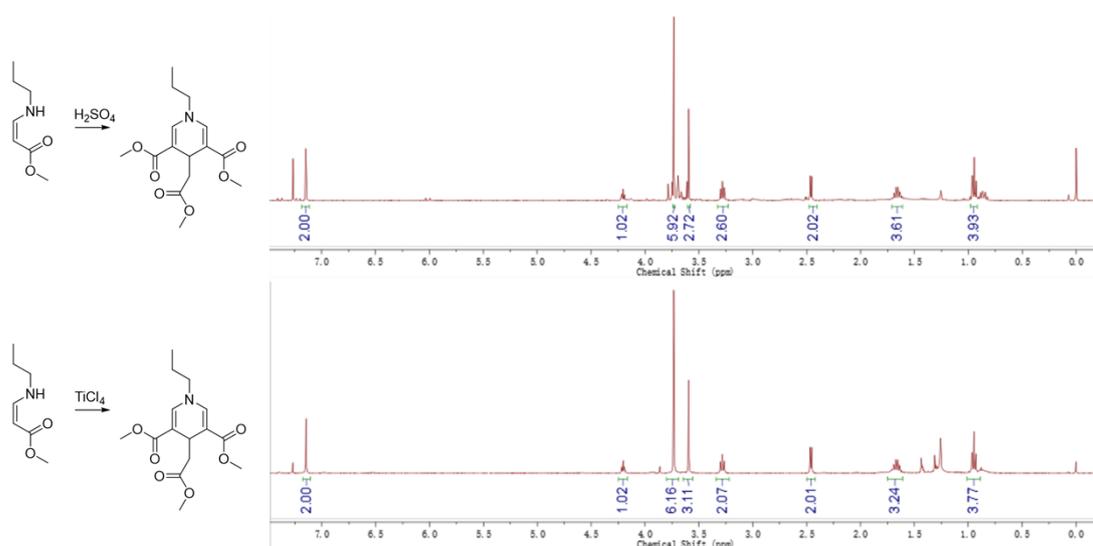


Fig. S2. The ¹H NMR spectrum (in CDCl₃) of compound DHPy synthesized in the presence of concentrated H₂SO₄ catalysis (up) and TiCl₄ catalysis (down).

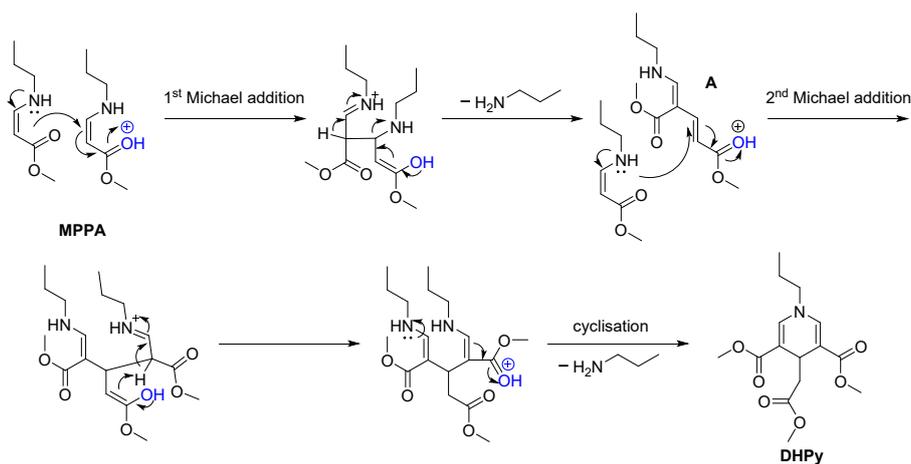


Fig. S3. Plausible mechanism of DHPy formation.

Acid-Responsive Properties of MPAA

Table S1. Photophysical data of MPAA before and after H₂SO₄ treatment. ^a

substrate	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)
MPAA	254	460	5.2
DHPy	374	455 (493) ^b	40.4 (9.0) ^b

^a Compounds MPAA and DHPy were dispersed in an aqueous medium. ^bThe maximum emission peak and fluorescence quantum yield of oily compound DHPy without dispersion in any solvent are shown in parentheses.

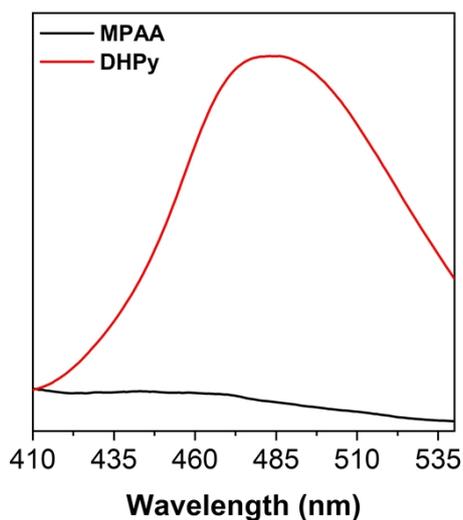
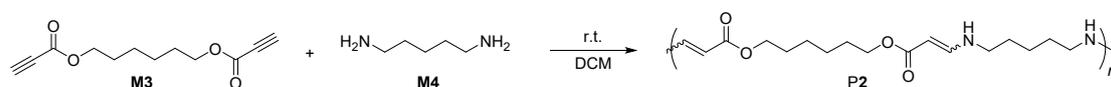


Fig. S4. The comparative fluorescence spectrum of MPAA and DHPy.

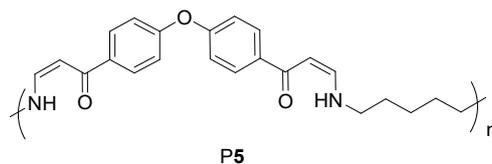
Preparation for Polymers

The preparation and characterization of click polymers follow the method in literature. Without additional notes, all the polymerization reactions were conducted under a nitrogen atmosphere using standard Schlenk technique. A typical procedure of the polymerization of **P2** are given below as examples (Scheme S5).



Scheme S5. Preparation of **P2**.

22.2 mg (0.1 mmol) of monomer **M3** was added into a 10 mL polymerization tube and dissolved in 2 mL of tetrahydrofuran (THF), followed by the addition of 11.7 μ L (0.1 mmol) of monomer **M4**. After stirring at room temperature for 2 h, the reaction mixture was slowly added dropwise into 125 mL of rapidly stirred *n*-hexane. The precipitated polymer was collected by filtration, washed with *n*-hexane, and dried under vacuum to constant weight, yielding a white polymer product **P2** with a yield of 86%. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.93 – 7.69 (m, N–H), 7.48 (m,



P5. Slightly yellow solid was obtained in 93% yield. FT-IR (KBr disk), ν (cm^{-1}): 3267, 3056, 2934, 2860, 1631, 1588, 1540, 1480, 1381, 1279, 1236, 1159, 1054, 1008, 880, 848, 774, 730. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 10.44 – 10.20 (m, 2H), 7.87 (d, 4H), 7.03 (d, 4H), 6.97 – 6.88 (m, 2H), 5.65 (d, $J = 7.4$ Hz, 2H), 3.28 (d, 4H), 1.70 – 1.57 (m, 4H), 1.47 (d, 2H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 188.77, 159.00, 154.23, 135.23, 129.06, 118.49, 89.87, 49.04, 30.74, 23.62.

Table S2. molecular weight characterization of polymers.^a

entry	M_n	M_w	D^b
P1	10400	15800	1.51
P2	13500	23800	1.77
P3	20200	35200	1.75
P4	9500	16300	1.72
P5 ^c	6800	8700	1.28

^a Determined by gel-permeation chromatography (GPC) in *N,N*-dimethylformamide (DMF) containing 0.05 M LiBr using linear PMMA for calibration. ^b D = dispersity. ^c Soluble part in DMF.

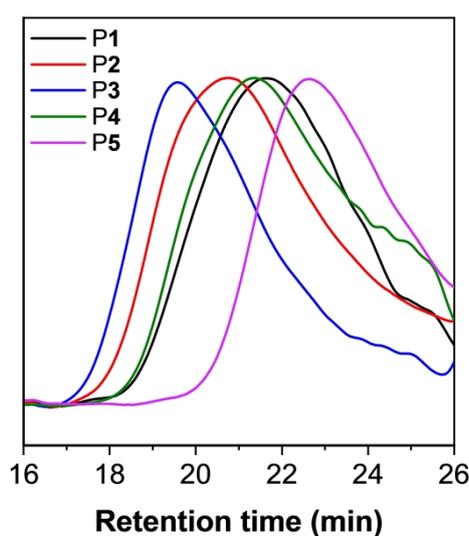


Fig. S5. GPC trace of the polymers determined by gel permeation chromatography in DMF containing 0.05 M LiBr using linear PMMA for calibration.

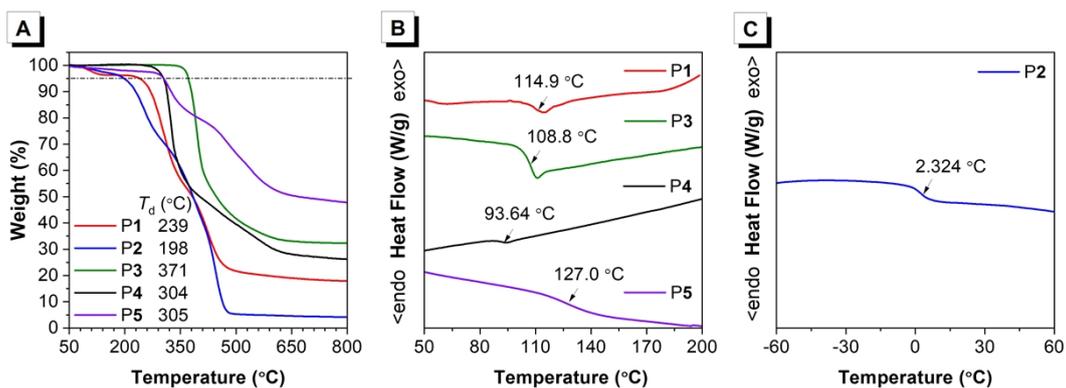


Fig. S6. Thermal stability of the polymers. (A) Thermal gravimetric analysis (TGA) thermograms of polymers under nitrogen; (B-C) Differential scanning calorimetry (DSC) grams of polymers under nitrogen.

Acid-Responsive Properties of Polymers

A typical procedure of the acidification reaction of P1 is given below as example: 0.2 mL of concentrated sulfuric acid was slowly added onto polymer P1 (40.8 mg, 0.1 mmol). After the reaction for 2 h, a large amount of water was added to dilute the mixture. The insoluble product was collected by filtration, washed with water, and yielded a light-yellow polymer exhibiting blue-green fluorescence, with a yield of 96%.

Table S3. Photophysical data of polymers P1 and P2 before and after H₂SO₄ treatment.^a

substrate	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)
P1	290	396	1.8
P1 + H ₂ SO ₄	290	463	4.2
P2	282	467	1.8
P2 + H ₂ SO ₄	290	477	6.5

^a The polymers were tested in a thin film.

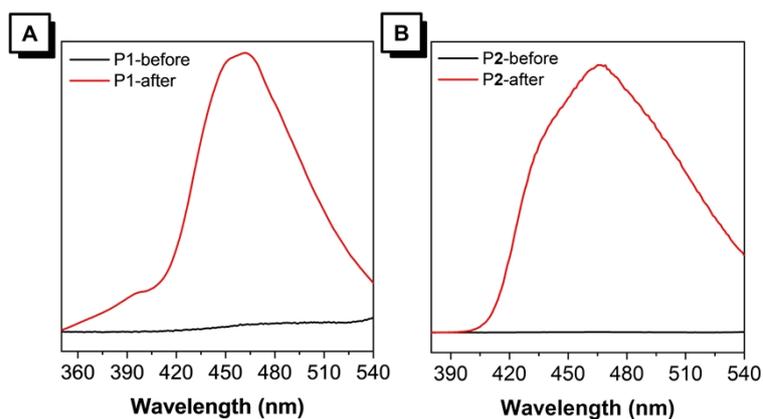


Fig. S7. The comparative fluorescence spectrum of the dihydropyridine derivative with their corresponding β -aminoacrylate precursors (P1 and P2).

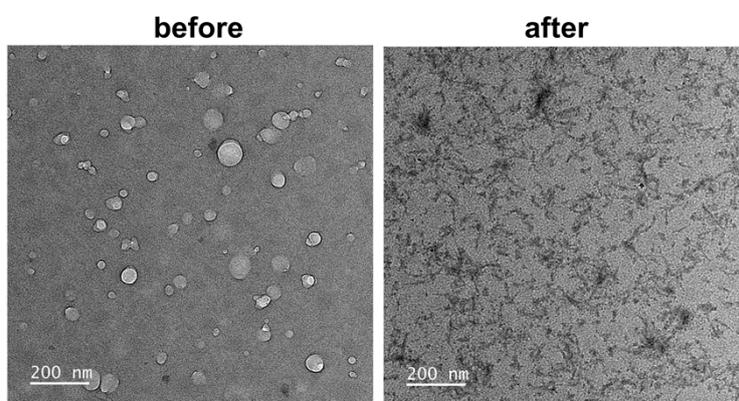


Fig. S8. Transmission electron microscope (TEM) photos of the suspension of polymer P2 before and after 3.6 M H_2SO_4 treatment.

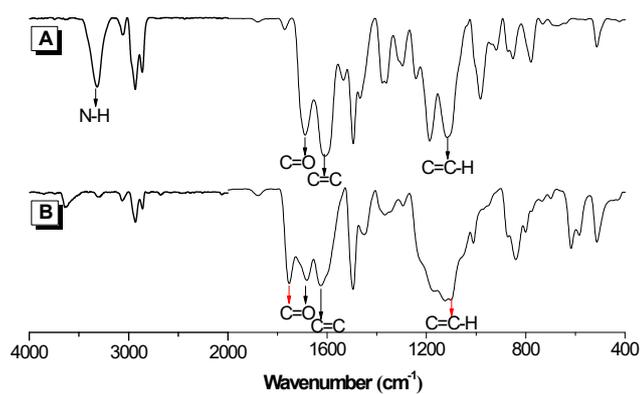


Fig. S9. FT-IR spectra of P1 (A) before and (B) after treated with sulfuric acid.

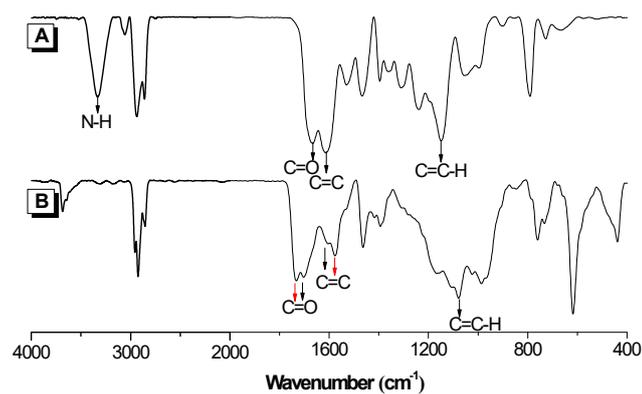


Fig. S10. FT-IR spectra of P2 (A) before and (B) after treated with sulfuric acid.

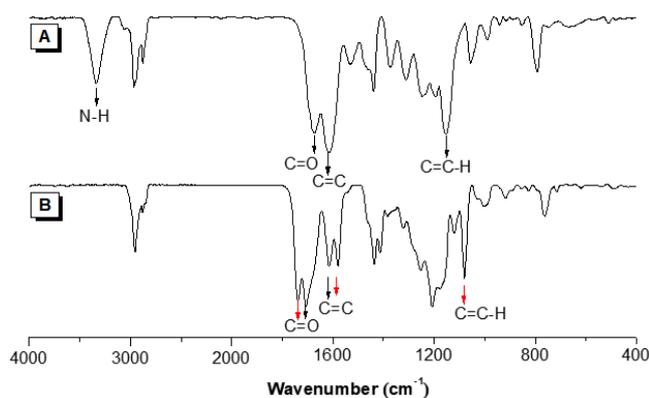


Fig. S11. FT-IR spectra of model compound MPAA (A) before and (B) after treated with sulfuric acid.

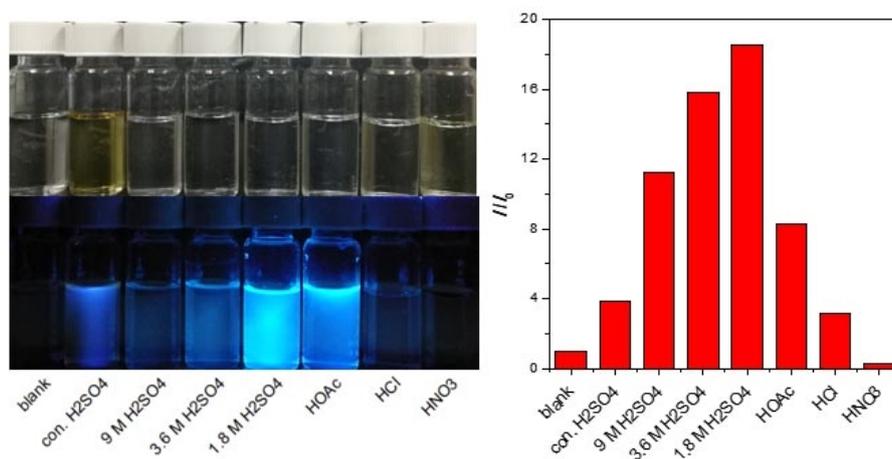


Fig. S12. Fluorescence “turn-on” effects of 50 μ M DHPy suspended in different acids (DMF/H₂O=10:90) for 2 h and corresponding fluorescence intensity statistics.

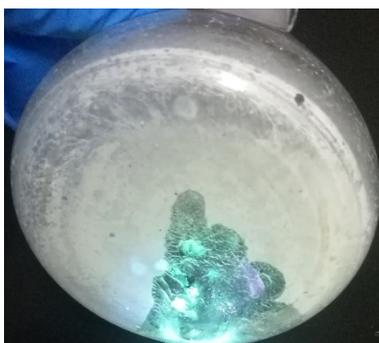


Fig. S13. Polymer film of P1 before (white area) after (green-blue luminescent area) treated with H₂SO₄.

References

- 1.(a) X. Chen, T. Bai, R. Hu, B. Song, L. Lu, J. Ling, A. Qin and B. Z. Tang, *Macromolecules*, 2020, **53**, 2516–2525; (b) B. He, H. Su, T. Bai, Y. Wu, S. Li, M. Gao, R. Hu, Z. Zhao, A. Qin, J. Ling and B. Z. Tang, *J. Am. Chem. Soc.*, 2017, **139**, 5437-5443; (c) X. Chen, A. Qin and B. Z. Tang. *Green Chem.*, 2024, **26**, 857-865.
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Additional Data

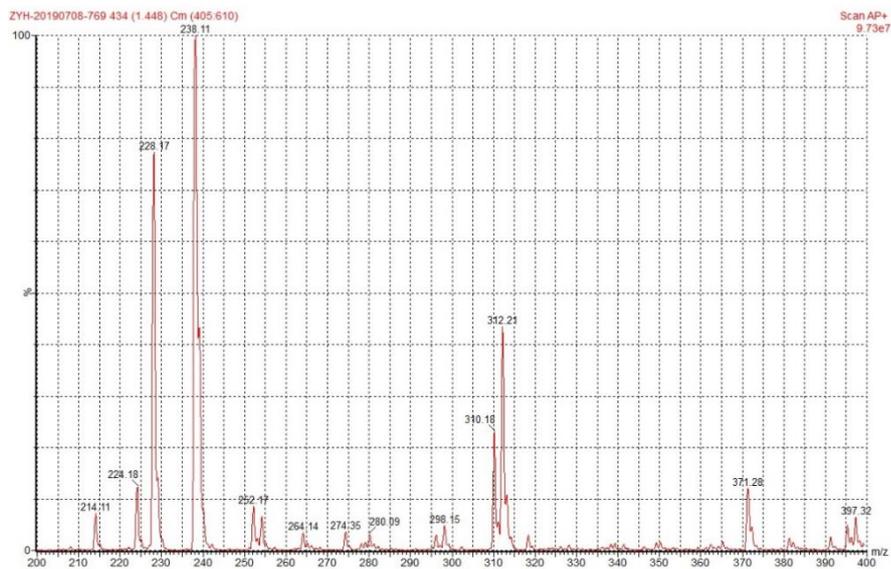


Fig. S14. Liquid chromatography-mass spectrum of compound DHPy.