Electronic Supplementary Information

Anionic Conjugated Polytriazole: Direct Preparation, Aggregation-enhanced Emission, and Highly Efficient Al^{3+} Sensing

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Contents

General Information

Materials and Instrumentation. Chemicals, reagents, and solvents used in this work were all purchased from J&K, TCI, Alfa and Aldrich, unless otherwise specified. THF was purified by the simple distillation from sodium benzophenone ketyl in an atmosphere of dry nitrogen immediately prior to use. Other solvents were purified by the standard procedures.

^{1}H NMR spectra were measured on a DMX-500 spectrometer (Bruker) in DMSO-d_6 using TMS (δ = 0) as the internal standard. IR spectra were taken on a Vector 22 spectrometer (Bruker). UV−vis spectra were measured on a Varian VARY 100 Bio UV−vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Thermal stability was evaluated by taking thermograms on Pyris 1 TGA at 10 °C/min under nitrogen and air respectively. Absolute quantum yield was measured on a HAMAMARSU C11347-11Quantaurus-QY. Relative number (M_n) and weight average (M_w) molecular weights and polydispersity indices (PDI, M_w/M_n) of the polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with refractive index (RI) detector, using a set of monodisperse poly(methyl methacrylate) (PMMA) as calibration standards and DMF as the eluents at a flow rate of 1.0 mL/min.

2. Synthetic Procedures

Polymer Synthesis.

The polymerization reaction was carried out under nitrogen using the standard Schlenk technique in a vacuum line system. Typical experimental procedure for the alkynyl-azide click polymerization

(AACP) is given below.

Into a 10 mL Schlenk tube with a stopcock in the side arm were placed **1** (32.2 mg, 0.06 mmol) and **2** (22.8 mg, 0.06 mmol). The tube was evacuated and refilled with dry nitrogen three times through the side arm. Freshly distilled DMF (2.5 mL) was injected into the tube to dissolve the monomers, followed by the freshly prepared aqueous solutions of $CuSO_4$ (1 M, 1.5 μL) and sodium ascorbate (SA, 1 M, 3 μL). The color of the solution turned to light yellow, and then yellow. After stirring at 60 °C for 6 h, the reaction mixture was added dropwise to into 200 mL of hexane/chloroform/methanol (3:3:2) mixture through a cotton filter under stirring. The precipitates were allowed to stand overnight and then collected by filtration. P**I** was obtained in 98.9% yield as a yellow powder. M_w 181 000; M_w/M_n 1.67. IR (thin film), v (cm^{-1}): 3100, 2910, 2100, 1650, 1492, 1438, 1400, 1210, 1085, 1015, 980, 700, 680. ^{1}H NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 9.24 (s, 2H; N-C*H*), 8.36 (d, 4H; Ar-*H*), 8.24 (m, 2H), 7.96 (d, 2H), 7.78 (d, 2H), 7.16 (d, 2H; R=C*H*), 7.11 (m, 14H; Ar-*H*). ^{13}C NMR (125 MHz, DMSO-d_6), δ (ppm): 162.5, 143.5, 143, 140.7, 140.5, 135.4, 135, 131, 130.4, 130, 125.2, 127, 127.9, 128, 120.2 119.5, 118.4.

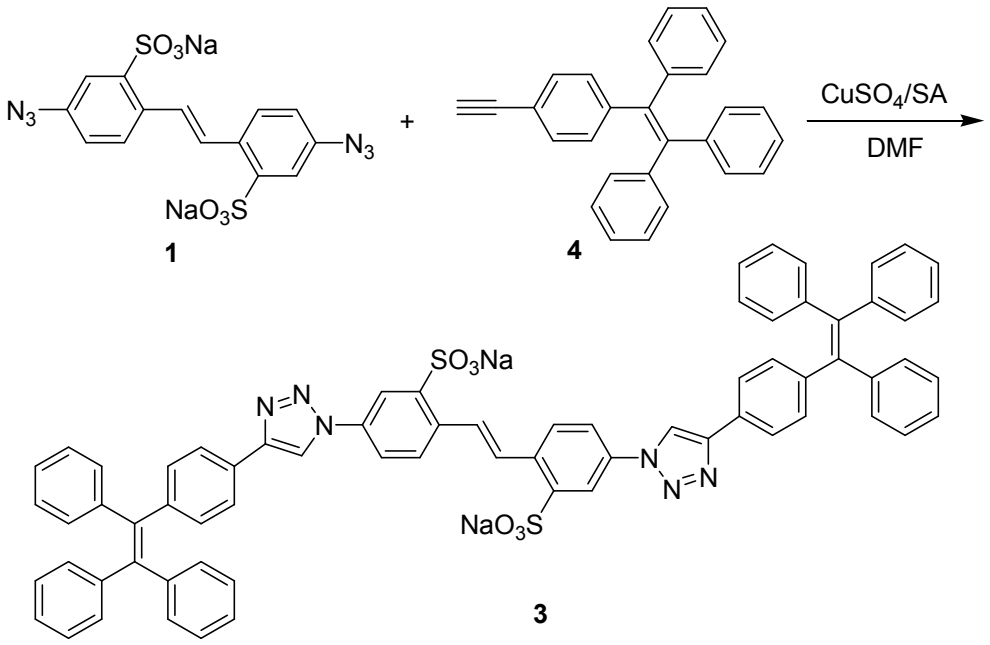
Preparation of Model Compound 3.

The click reaction of **1** and **4** was carried out under the conditions similar to that of the polymerization. The color of the solution turned from clear to light yellow after $CuSO_4$/SA was added into it. After stirring at 60 °C for 24 h, the reaction solution was poured into water. The product was isolated via centrifugation. The collect solids were washed with THF three times and yellow powder **3** was obtained in 95% yield after dryness. FT-IR (KBr) v (cm^{-1}): 3080, 2950, 2110, 1660, 1610, 1495, 1430, 1300, 1200, 1080, 1030, 980, 690, 610. ^{1}H NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 9.24 (s, 2H; N-CH), 8.36 (s, 2H; Ar-H), 8.24 (d, 4H), 7.96 (d, 4H), 7.78 (d, 4H), 7.16 (m, 30H; Ar-H), 7.05 (d, 2H). ^{13}C NMR (125 MHz, DMSO-d_6), δ (ppm): 148, 145.6, 143.5,

141.7, 136.8, 133.5, 132.8, 131.4, 129.8, 129, 127.7, 126.2.

Preparation of polymer aggregates

A stock solution of P**I** in DMF (0.1 mM) was first prepared. Aliquots of this stock solution were transferred into volumetric flasks (10 mL), into which appropriate volumes of DMF and THF were added dropwise under vigorous stirring to give 10 μM solutions with different THF contents (f_{THF} = 0~90 vol %). UV and PL spectra were measured immediately after the solutions were prepared.



Scheme S1. Synthetic route to model compound **3**.

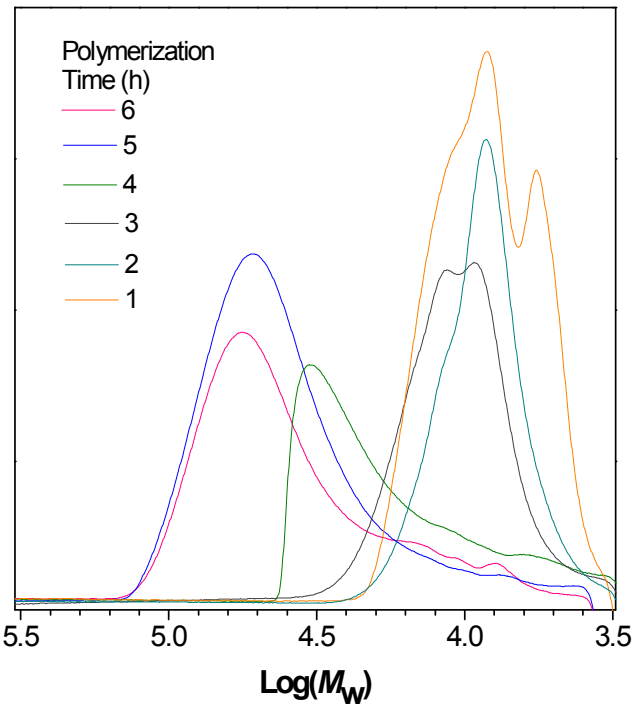


Figure S1. GPC curves of P**I** recorded in DMF containing 0.05% LiBr using a set of monodisperse poly(methyl methacrylate) calibration.

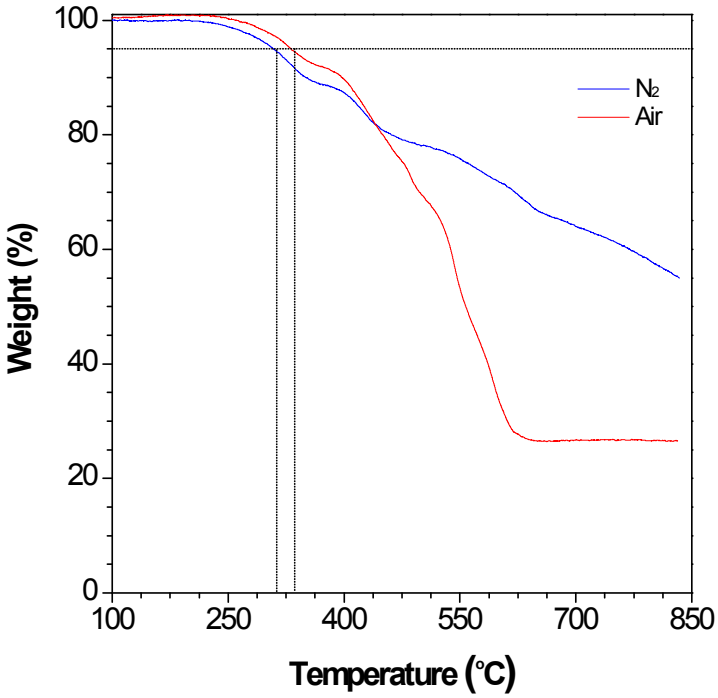


Figure S2. TGA thermograms of P**I** recorded at a heating rate of 10 °C/min.

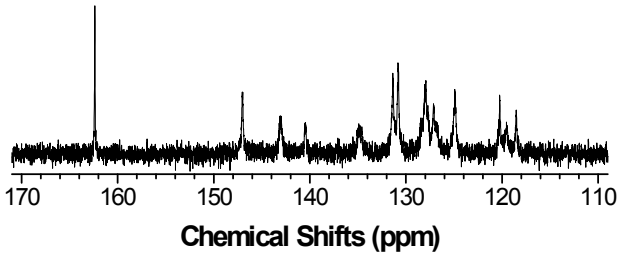


Figure S3. ^{13}C-NMR spectrum of P**I** in DMSO-d_6.

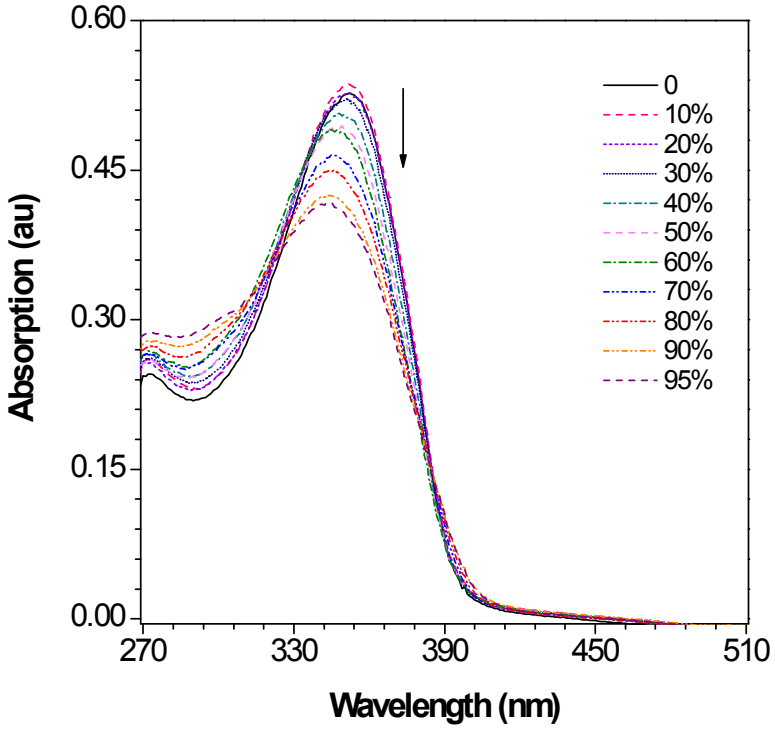


Figure S4. UV-vis spectra of P**I** in DMF and DMF/THF mixtures. Concentration: 5μM.

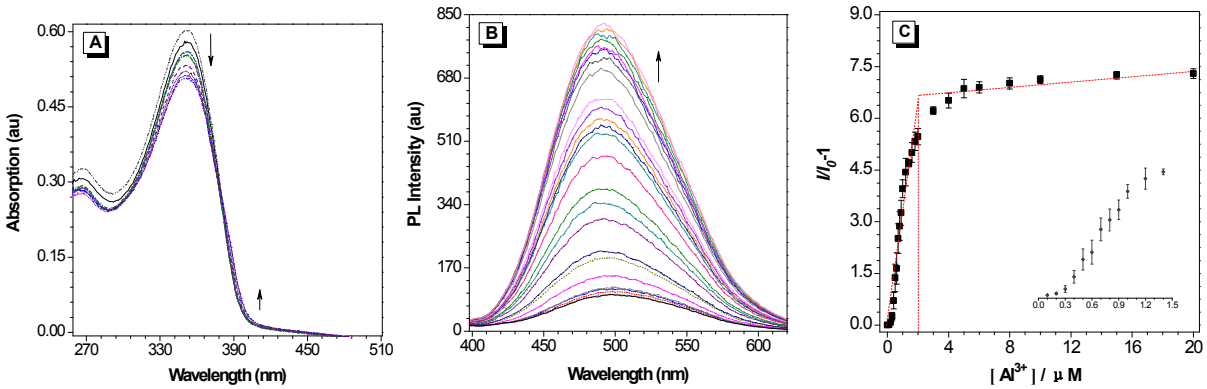


Figure S5. (A) UV-vis spectra of P**I** with different equivalents (varied from 0.1 to 20) of Al^{3+} in DMSO/water mixtures (10 μM, with water fraction 10%). (B) PL spectra of P**I** with different equivalents (varies from 0.1 to 20) of Al^{3+} in DMSO/water mixture solvents (10 μM, with water fraction 10%); λ_{ex}: 346 nm. (C) Plot of P**I** solution response to different equivalents (varies from 0.1 to 20) of Al^{3+} in DMSO/water mixture solvents (10 μM, with water fraction 10%).

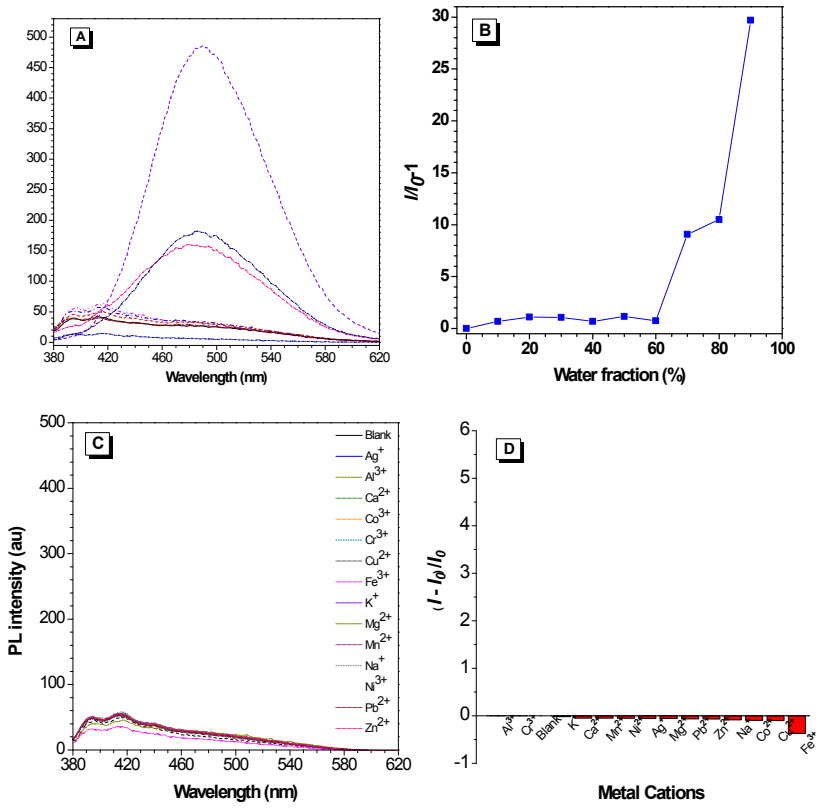


Figure S6. (A) PL spectra of **3** in DMF/water mixtures with different water fractions. Concentration: 5 μM. λ_{ex}: 346 nm. (B) Plot of I_0/I-1 of **3** versus water fraction in DMF/water mixtures. I_0 = PL intensity at 486 nm of **3** in DMF solution; I = PL intensity at 486 nm of **3** in DMF/water mixtures. (C) PL spectra of **3** in DMSO/water mixture (10 μM, 10 % water) in the presence of 10 equivalents of different metal cations. λ_{ex}: 346 nm. (D) The change of relative PL intensity of **3** upon addition metal cations in DMSO/water mixture with water fraction of 10%.

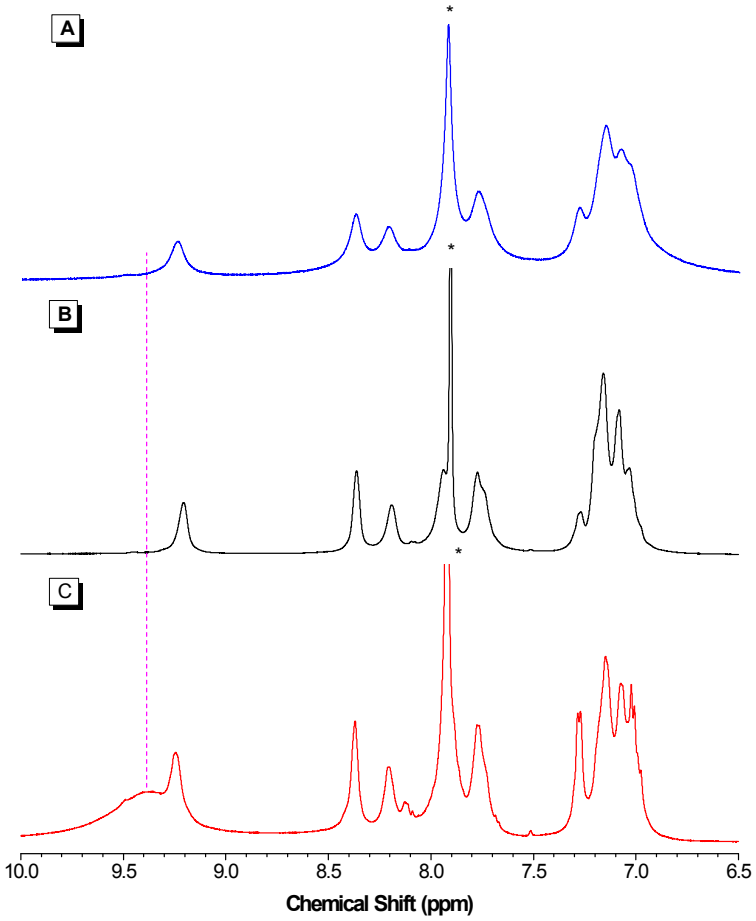


Figure S7. ^{1}H NMR spectra of (A) P**I** + Zn^{2+}, (B) P**I** and (C) P**I** + Al^{3+} in DMSO-d_6/D_2O (10:1, v/v). [P**I**/M] = 1:2. The solvents were marked in asterisks.