

Poly(arylene ynonylene) with an aggregation-enhanced emission characteristic: a fluorescent sensor for both hydrazine and explosive detection†

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A high molecular weight poly(arylene ynonylene) with an aggregation-enhanced emission characteristic was synthesized in high yield by a newly developed polymerization route. Its emission can be turned 'on' by hydrazine, as well as 'off' by picric acid, demonstrating the first fluorescent sensor that works for both hydrazine and explosives detection.

The detection of explosives has attracted much interest because of the increased use of explosives in terrorism acts.¹ Besides being famous as a high-energy propellant in rockets and spacecraft, hydrazine is widely used in industrial and agricultural production.² On the other hand, it is a carcinogen, can do harm to the lungs, liver and respiratory tract, and has a long-term effect on the central nervous system.² Its facile detection is thus relevant to homeland security. Spectrophotometric and electrochemical methods are generally used for hydrazine sensing, but they lack sensitivity and are power-consuming.³ The development of new methods for hydrazine detection is therefore of both academic importance and practical implication.

Among various analytical techniques, fluorescence-based methods possess high sensitivity, low background noise and wide dynamic ranges.¹ So far, many fluorescent probes for explosives have been developed based on the mechanism of photo-induced energy transfer,¹ whereas only limited fluorescent sensors have been constructed for hydrazine detection.⁴ On the other hand, to the best of our knowledge, there is no single material reported in the literature that can detect both hydrazine and explosives.

Conjugated polymers are promising candidates as fluorescent sensors, due to their amplified response and superior sensitivity to analytes, in comparison to their low molar mass congeners.⁵ Their sensing performance, however, is often deteriorated by the intrinsic autoaggregation of their chains, which interferes with the detection of analytes that induce the polymer strands to aggregate in solution. We recently observed a phenomenon of aggregation-induced emission in some propeller-shaped molecules.⁶ Instead of quenching, aggregate formation has boosted their fluorescence quantum yields, turning them from weak fluorophores into strong emitters. Polymers carrying such luminogens emit intensely in the aggregated state and can be utilized as sensitive 'turn off' fluorescent sensors for explosives, such as picric acid (PA).⁷

Terminal arylacetylenes and aroyl chlorides can undergo coupling reactions in the presence of palladium catalysts to furnish arylynes.⁸ While this reaction has been utilized by synthetic organic chemists to prepare alkyne derivatives, no attempt has been made to develop this reaction into a useful tool for the synthesis of new conjugated polymers. In this paper, we explored such a possibility and show that the new poly(arylene ynonylene) constructed from tetraphenylethene (TPE) serves as a fluorescent sensor for both hydrazine and explosives, which is extraordinary, if not without precedence.

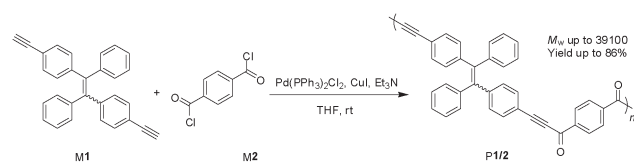
The TPE-containing diyne **M1** was synthesized according to our previous publication,⁹ while **M2** was commercially available (Scheme 1). Their polymerization was initiated by Pd(PPh₃)₂Cl₂ and CuI in a basic medium. To search for optimal conditions, we have investigated the effects of catalyst concentration (Table S1,

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Scheme 1 The synthesis of tetraphenylethene-functionalized poly(arylene ynonylene).

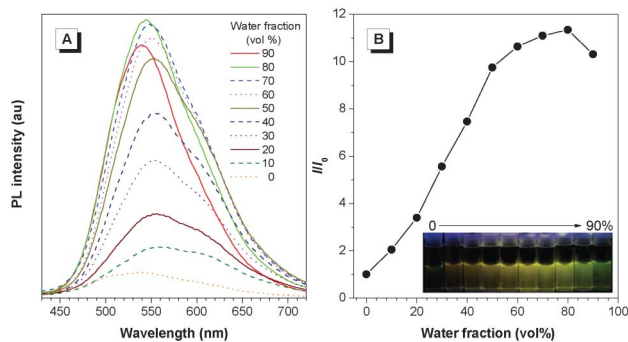


Fig. 1 (A) PL spectra of P1/2 in THF–water mixtures with different water fractions at room temperature. (B) Plot of the relative PL intensity (I/I_0) versus the composition of the THF–water mixture of P1/2. Concentration: 10^{-5} M; excitation wavelength: 360 nm. Inset: fluorescent photographs of a THF solution and THF–water mixtures of P1/2 with different water fractions taken under 365 nm UV irradiation.

ESI† entry no. 1–3), reaction time (entry no. 4–6), sequence of monomer addition (entry no. 7–8) and organic base concentration (entry no. 9–11) on the polymerization. We found that the reaction conducted at a catalyst concentration of 5 mM and with one equivalent of triethylamine, with prior addition of M1, proceeded smoothly, affording P1/2 with good solubility and high molecular weight in 70% yield (Table S1, ESI† entry no. 7). To assist with the structural assignment, we carried out a model reaction of M3⁹ with benzoyl chloride under the same experimental conditions, which gave MC4 in a high yield (Scheme S1, ESI†). The IR and NMR spectra of P1/2 show satisfactory analysis data corresponding to its molecular structure (Fig. S1–S3, ESI†). The polymer is thermally stable, losing little of its weight at 376 °C under nitrogen and at 390 °C in air (Fig. S4, ESI†).

Compound P1/2 absorbs at 366 nm in diluted THF solution (Fig. S5, ESI†). Upon photoexcitation, it emits a yellow light at 550 nm (Fig. 1A), which is 80 nm red-shifted from that of M1 due to the enhanced conjugation by the electronic communication between the TPE unit and the ynonephenyl group. The addition of water to the tetrahydrofuran (THF) solution has enhanced the emission intensity and slightly blue-shifted the spectrum. The higher the water content, the stronger is the light emission. From the initial THF solution to a 90% aqueous mixture, the emission intensity rises by more than 10-fold (Fig. 1B). Since P1/2 is insoluble in water, its chains must have been aggregated in aqueous mixtures with high water content. Clearly, the photoluminescence (PL) of P1/2 is enhanced by aggregate formation or in other words, P1/2 displays a novel phenomenon of aggregation-enhanced emission (AEE).^{6,8} The fluorescent photograph of the polymer in THF solution and aqueous mixtures shown in the inset also demonstrates its AEE feature.

The ynone unit is known as a fluorescence quenching site as well as a reactive moiety for nucleophile addition. Since hydrazine is an extremely reactive binucleophile, it may react with the ynone units of P1/2, changing its electronic property and hence alter its emission behavior.¹⁰ In other words, P1/2 may be utilized as a fluorescent probe for hydrazine detection. Indeed, with the gradual addition of hydrazine into a dimethylformamide (DMF)

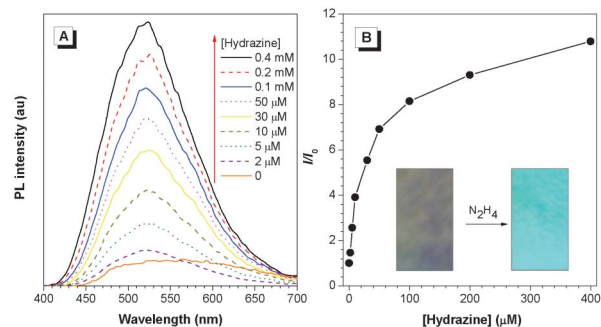


Fig. 2 (A) PL spectra of P1/2 in DMF solutions containing different amounts of hydrazine. (B) Plot of the relative PL intensity (I/I_0) versus the hydrazine concentration in a DMF solution of P1/2. I_0 = peak intensity at [PA] = 0. Concentration: 1 mM; excitation wavelength: 360 nm. Inset: photographs of P1/2 adsorbed on filter paper before and after being dipped into aqueous hydrazine solution (~ 10.3 M) taken under 365 nm UV irradiation.

solution of P1/2, the emission becomes progressively stronger, accompanied by a blue-shift in the PL maximum (Fig. 2). The detection can be observed at a hydrazine concentration as low as 2 ppm. The sensing is also workable in the solid state. As illustrated in the inset, the filter paper adsorbed with P1/2 fades in colour and lights up instantly from weak yellow to strong green emission after being dipped into an aqueous hydrazine solution (10.3 M). The contrast is so large that it can be discernible readily by the naked eye. Such a result is much better than the previous system, in which the emission intensity of the fluorescent polymer film increases merely by 2-fold, upon exposure to hydrazine vapour.⁴ A time course study shows that the detection is fast and efficient: the PL intensity rises gradually with time and becomes saturated at ~ 10 min when 5 μ L of a hydrazine monohydrate solution (20.6 M) is added to 1 mM of a DMF solution of P1/2 (Fig. 3).

To understand the hydrazine detection mechanism, we analyzed the reaction product at different reaction times by IR spectroscopy. The absorption peaks associated with C=C and C=O stretching vibrations of P1/2 become weaker progressively with time and disappear completely after ~ 20 min (Fig. S6, ESI†). This result not only demonstrates the high efficiency of such a reaction

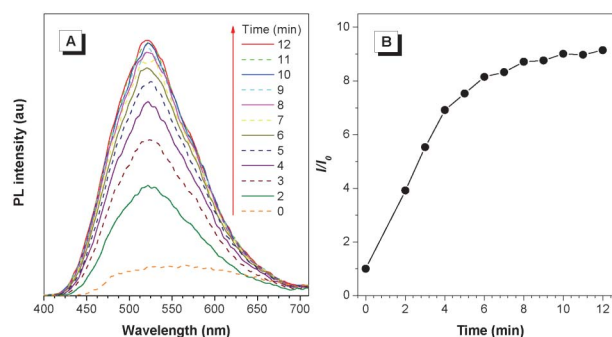
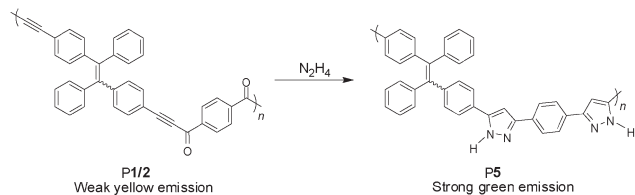


Fig. 3 (A) PL spectra of P1/2 in a DMF solution containing 5 μ L hydrazine at different times. (B) Change in the relative PL intensity (I/I_0) of a DMF solution of P1/2 containing 5 μ L hydrazine with time. I_0 = peak intensity at [PA] = 0. Polymer concentration: 1 mM; excitation wavelength: 360 nm.



Scheme 2 'Click' reaction of P1/2 with hydrazine.

but also suggests that the modification occurs readily at the ynone group. We intended to characterize the post-polymeric product by NMR spectroscopy, but its low solubility in common solvents prevented us from performing such an investigation. We thus carried out a model reaction of MC4 with hydrazine, which afforded MC6 in a high yield. Its ^1H and ^{13}C NMR spectra (Fig. S7 and S8, ESI†) reveal that the ynone group has been cyclized into a pyrazole ring by reaction with hydrazine, but does not affect the TPE unit (Schemes 2 and S2, ESI†).

Compound P1/2 is capable of reacting with the derivatives of hydrazine such as benzylhydrazine and 2-hydrazinopyridine at much slower rates. Nucleophiles such as amines and thiols may undergo nucleophilic addition with P1/2, only converting its triple bond to a vinyl functionality and having minimal affect on its absorption and emission, instead of the blue-shift as observed in Fig. 2. Thus, the hydrazine sensing is not only sensitive but also somehow selective, though the process is irreversible. The conjugation of P5 is lower than P1/2 due to the steric repulsion between the TPE and pyrazole units (Fig. S5, ESI†). However, it emits more intensely because the emission quenching effect of the ynone moiety no longer exists.

Compound P1/2 can also function as a sensitive fluorescent chemosensor for PA. As shown in Fig. 4A, with a gradual addition of PA into the THF–water mixture (1/9 v/v) of P1/2, its emission is lowered progressively. Even at a low PA concentration of 1 ppm, obvious PL annihilation was observed. Similar emission quenching was found when the detection was carried out in a THF solution. Stern–Volmer plots of the relative PL intensity *versus* PA concentration show upward-bending curves, instead of straight

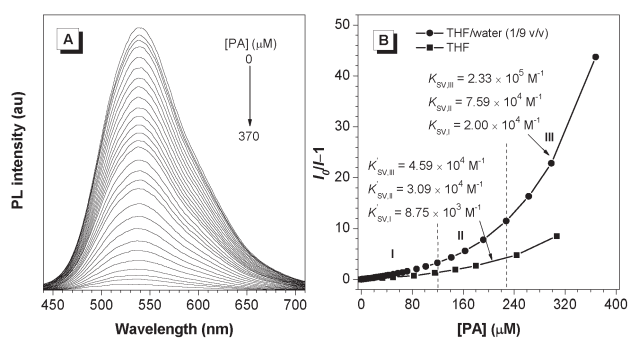


Fig. 4 (A) PL spectra of P1/2 in THF–water mixtures (1/9 v/v) with different concentrations of picric acid (PA) at room temperature. (B) Plots of $(I_0/I-1)$ values *versus* PA concentrations in a THF–water mixture (1/9 v/v) and a THF solution of P1/2. I_0 = peak intensity at $[\text{PA}] = 0$. Concentration: 10^{-5} M; excitation wavelength: 360 nm.

lines, indicative of a superamplification effect. Large quenching constants up to $2.33 \times 10^5 \text{ M}^{-1}$ are deduced from the plots (Fig. 4B), whose values are much higher than those of polysiloles and polygermoles reported previously in solutions.¹¹ The PA detection is more efficient when the measurement is carried out in a THF–water mixture, which is in some sense expected, because the polymer emits more intensely in the aggregated state due to its AEE characteristic. Moreover, its nanoaggregates possess a three-dimensional topological structure, which provides numerous internal voids for capturing analyte species and migration pathways to excitons.^{7,11} Since the PA molecules are not covalently bound to the polymer, the emission quenching process is reversible. As demonstrated in Fig. S9, ESI† the emission of P1/2 film coated on a glass slide can be turned 'off' and 'on' several times, by alternately dipping the plate into an aqueous PA solution and then washing with distilled water.

The nanoaggregates of P5 suspended in DMF–water mixture (2: 3 v/v) can also work as fluorescent PA sensors with a superamplification effect (Fig. S10A, ESI†). The sensitivity is even higher than that of P1/2, as revealed by the larger quenching constants (up to $1.09 \times 10^6 \text{ M}^{-1}$) calculated from the Stern–Volmer plot, shown in Fig. S10B, ESI†. This may be associated with its stronger light emission and greater overlapping between its emission spectrum and the absorption spectrum of PA (Fig. S11, ESI†), thus endowing it with a superior performance for PA detection than P1/2.

In conclusion, a new methodology for the synthesis of high molecular weight poly(arylene ynone) with an AEE characteristic in a high yield was developed. The polymer can simultaneously serve as both a 'light up' probe for the detection of hydrazine and a 'turn off' sensor for PA, with high sensitivity.

Acknowledgements

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References

- (a) J. Yinon, *Anal. Chem.*, 2003, **75**, 98 A; (b) S. W. Samuel III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339; (c) M. S. Meaney and V. L. McGuffin, *Anal. Bioanal. Chem.*, 2008, **391**, 2557; (d) J. S. Caygill, F. Davis and S. P. J. Higson, *Talanta*, 2012, **88**, 14.
- (a) J. Wang and L. Chen, *Anal. Chem.*, 1995, **67**, 3824; (b) D. L. Ellis, M. R. Zakin, L. S. Bernstein and M. F. Rubner, *Anal. Chem.*, 1996, **68**, 817; (c) A. Umar, M. M. Rahman and Y. B. Hahn, *Talanta*, 2009, **77**, 1376.
- (a) J. Mañes, P. Campillos, G. Font, H. Martre and P. Prognon, *Analyst*, 1987, **112**, 1183; (b) J. Wang and L. Chen, *Anal. Chem.*, 1995, **67**, 3824.

- 4 S. W. Thomas III and T. M. Swager, *Adv. Mater.*, 2006, **18**, 1047.
- 5 V. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605.
- 6 (a) J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (c) Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
- 7 (a) J. Liu, Y. Zhong, P. Lu, Y. N. Hong, Y. Yu, J. W. Y. Lam, M. Faisal, Y. Yu, K. S. Wong and B. Z. Tang, *Polym. Chem.*, 2010, **1**, 426; (b) J. Wang, J. Mei, W. Z. Yuan, P. Lu, A. J. Qin, J. Z. Sun, Y. G. Ma and B. Z. Tang, *J. Mater. Chem.*, 2011, **21**, 4056.
- 8 (a) D. A. Alonso, C. Najern and M. C. Pacheco, *J. Org. Chem.*, 2004, **69**, 1615; (b) L. Chen and C. Li, *Org. Lett.*, 2004, **6**, 3151.
- 9 (a) J. Z. Liu, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2009, **109**, 5799; (b) R. R. Hu, J. W. Y. Lam, J. Z. Liu, H. H. Y. Sung, I. D. Willians, Z. N. Yue, K. S. Wong, M. M. F. Yuen and B. Z. Tang, *Polym. Chem.*, 2012, **3**, 1481.
- 10 (a) B. Willy and T. J. J. Müller, *Eur. J. Org. Chem.*, 2008, **24**, 4157; (b) H. L. Liu, H. F. Jjiang, M. Zhang, W. J. Yao, Q. H. Zhu and Z. Tang, *Tetrahedron Lett.*, 2008, **49**, 3805.
- 11 H. Sohn, M. J. Sailor, D. Magde and W. C. Troglor, *J. Am. Chem. Soc.*, 2003, **125**, 3821.