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Water-soluble anionic fluorophores from truxene

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ABSTRACT

Two new water-soluble fluorophores are synthesized from truxene and ester-substituted aryl acetylenes. The truxene core is decorated by 2-(2′-methoxy)ethoxyethyl groups to enhance the hydrophilicity of these fluorophores as well as to prevent the aggregation by π-stacking in aqueous media. The conjugated structures are assembled by iodination of the truxene core and subsequent Sonogashira coupling with aryl acetylenes. Upon the hydrolysis of the ester groups, water-soluble fluorophores are obtained in good to excellent yield (30–71% for 3 steps). A photophysical investigation reveals that these compounds exhibit strong fluorescence signals (quantum yield 46–63%) with maximum emission wavelength around 390–400 nm in aqueous phosphate buffer. Preliminary screening on sensing application shows that their fluorescent signals can be selectively quenched by porphyrin-containing metalloproteins.

1. Introduction

Fluorescence signal transduction has been widely used as a selective and sensitive method for the detection of chemical and biological substances [1–3]. Conjugated polyelectrolytes have usually served this purpose due to their tunable optoelectronic properties and good water solubility. By a signal amplification mechanism in which the exciton can migrate along the conjugated backbone, polymeric fluorophores are more sensitive toward the analytes than their small molecule analogs [4–9]. Linear poly(-phenyleneethynylene) [8] and poly(fluorene) [9] are among the major classes of compound used as fluorescence signal transducers. They are usually prepared by Pd-catalyzed reactions such as Heck [10], Suzuki [11], and Sonogashira coupling [12]. In most cases, these polymers are polydispersed and their molecular weight distribution or degree of polymerization depends variably on the conditions in which they are produced. Furthermore, their optical properties cannot be correlated with a high degree of certainty to their three-dimensional structure due to their random coil conformation [13]. In comparison with linear polymers, dendrimers usually possess more predictable geometry as well as a monodispersity achieved by stepwise synthetic routes [14]. As a result, fluorescent dendrimers have recently been of growing interest in the development of chemical and biological sensors [15–17].

During the course of our research program on design and synthesis of dendritic polyelectrolytes, we have established the synthesis and applications of a polyanionic dendrimer as a selective fluorescence sensor for mercuric ion [18]. Most recently, we demonstrated the use of variously charged dendritic polyelectrolytes in sensor array along with a multivariate statistical analysis for protein discrimination [19]. In the development of π-conjugated materials as fluorescent signal transducers via quenching process, high quantum efficiencies of the fluorophores are challenging and desirable, especially for application in aqueous system. In the present work, we report the design and synthesis of a new class of water-soluble fluorophores containing a truxene core which showed high quantum efficiency and selective fluorescence quenching by porphyrin-containing metalloproteins.

Truxene or 10,15-dihydro-5*H*-diindeno[1,2-*α*;1′,2′-*c*]-fluorene has been used as a photoactive moiety in materials for organic light-emitting diodes and phosphorescent metal complexes [20–24]. With its molecular rigidity and a highly emissive property, we chose to incorporate a truxene unit into our target molecules **1** and **2** (Fig. 1) and demonstrate the first application of this fluorescent building block as water-soluble sensing materials. However, the structure of truxene is highly hydrophobic and relatively planar which can lead to a poor water solubility and lower quantum efficiency due to aggregation. We therefore opted to install six

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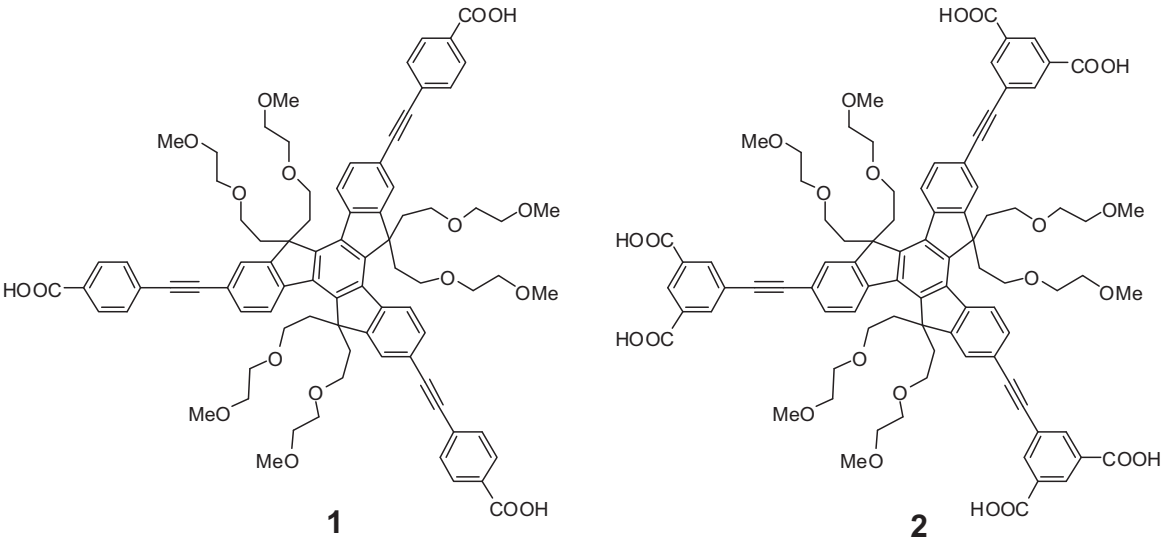


Fig. 1. Structure of fluorophores **1** and **2**.

hydrophilic chains of 2-(2′-methoxy)ethoxyethyl at the methylene positions of truxene. This structural modification should facilitate the water solubility and prevent molecular aggregation by π-stacking. Three phenylethynylene moieties were connected to the truxene core to extend the π-conjugated system and shift the emission wavelength into the visible region. The ionizable carboxylic acid groups installed at the peripheries could promote the solubility in water and serve as interaction sites for analytes.

2. Experimental

2.1. Chemicals and instruments

The starting materials and reagents were purchased from commercial sources and used without further purification. All ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury NMR spectrometer, which operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei (Varian Company, CA, USA). Mass spectra were recorded on a Microflex MALDI-TOF mass spectrometer (Bruker Daltonics) using doubly recrystallized α-cyano-4-hydroxy cinnamic acid (CCA) and dithranol as a matrix.

2.2. Synthesis

2.2.1. Truxene (*4*)

A mixture of 3-phenylpropionic acid (**3**) (10.0 g, 66.7 mmol) and polyphosphoric acid (50 g) was heated at 60–65 °C for 60 min under nitrogen atmosphere. Water (5 mL) was then added to the reaction and temperature was raised to 160 °C and maintained for 3 h. After the reaction was allowed to cool to room temperature, the mixture was poured into ice/water and gray powder was filtered and washed with water. The product was purified by column chromatography on silica gel eluting with hexanes to yield **1** as light-yellow solid (4.3 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.97 (d, $J = 7.2$ Hz, 3H), 7.70 (d, $J = 7.6$ Hz, 3H), 7.51 (t, $J = 7.6$ Hz, 3H), 7.40 (t, 3H, $J = 7.6$ Hz, 3H) 4.29 (s, 6H).

2.2.2. 5, 5′, 10, 10′, 15, 15′-hexa-2-(2-methoxyethoxy)ethyltruxene (*5*)

To a stirred solution of **4** (0.10 g, 0.29 mmol) in DMF (10 ml) at 0 °C under nitrogen, NaH (0.09 g, 2.32 mmol) was added. Then the solution was allowed to warm to room temperature and stirred for 30 min, then 1-iodo-2-(2-methoxyethoxy)ethane (0.53 g, 2.32 mmol) was added. After stirring for 24 h, the mixture was poured into water and extracted with EtOAc. The volatile solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel eluting with EtOAc to yield **5** (182 mg, 66%) as white crystalline solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.34 (d, $J = 8.3$, 3H), 7.58 (d, $J = 8.3$ Hz, 3H), 7.41 (m, 6H), 3.19–3.28 (m, 36H), 3.06 (m, 12H), 2.50–2.72 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 151.5, 143.0, 138.1, 127.4, 127.3, 125.1, 122.8, 71.5, 69.7, 67.1, 58.8, 51.2, 36.0.

2.2.3. 2, 7, 12-Triiodo-5, 5′, 10, 10′, 15, 15′-hexa-2-(2-methoxyethoxy)ethyltruxene (*6*)

A solution of **5** (0.20 g, 0.20 mmol) in 20 ml of solvent mixture ($CH_3COOH : H_2SO_4 : H_2O : CCl_4 = 100 : 5 : 20 : 8$) was heated to 40 °C with stirring. After adding KIO_3 (0.05 g, 0.23 mmol) and I_2 (0.08 g, 0.32 mmol), the mixture was heated to 80 °C and stirred for 3 h. After the mixture was cooled to room temperature, it was poured into water and extracted with EtOAc. The volatile solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel eluting with EtOAc to yield **6** (0.26 g, 93%) as yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.97 (d, $J = 8.1$ Hz, 3H), 7.85 (s, 3H), 7.68 (d, $J = 8.1$, 3H), 3.01 (m, 18H), 2.63 (m,12H), 2.44 (m, 6H). ^{13}C NMR ($CDCl_3$, 400 MHz, ppm) δ 154.0, 143.5, 137.4, 137.3, 136.5, 132.4, 126.6, 93.5, 71.6, 69.9, 67.0, 58.9, 51.7, 35.8, 29.7.

2.2.4. Triester *7*

To a mixture of **6** (180 mg, 0.14 mmol), $PdCl_2(PPh_3)_2$ (8 mg, 0.01 mmol), CuI (6 mg, 0.02 mmol) in toluene 13 (mL) was added DBU 1 (mL) and the mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with EtOAc then filtered through a pad of silica gel. The filtrate was washed with water and the organic phase was dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with gradient solvents from ethyl acetate/hexane (1/2) to pure EtOAc to afford **7** as a yellow amorphous solid (0.18 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.34 (d, $J = 8.2$ Hz, 3H), 8.07 (d, $J = 8.4$ Hz, 6H), 7.78 (s, 3H), 7.67 (d, $J = 8.4$ Hz, 6H), 7.61 (d, $J = 8.2$, 3H), 3.94 (s, 9H), 3.09–3.28 (m, 48H), 2.58–2.76 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 166.5, 151.9, 144.5, 138.4, 137.7, 131.6, 131.0, 129.6, 128.5, 127.8, 126.2, 125.1, 121.8, 92.5, 90.0, 71.6, 69.9, 67.1, 58.9, 52.2, 51.6, 36.1.

*2.2.5. Hexaester **8***

A mixture of **6** (100 mg, 0.075 mmol), $PdCl_2(PPh_3)_2$ (3 mg, 0.004 mmol), CuI (2 mg, 0.008 mmol), in toluene 8 (mL) was added DBU 0.5 (mL) and the mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with EtOAc then filtered through a pad of silica gel. The filtrate was washed with water and the organic phase was dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with gradient solvents from ethyl acetate/hexane (1/2) to pure EtOAc to afford **8** as a yellow amorphous solid (52 mg, 43%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.67 (d, J = 1.5 Hz, 6H), 8.46 (d, 1.5 Hz, 6H), 8.36 (d, 8.4 Hz, 3H), 7.80 (s, 3H), 7.62 (d, 8.4 Hz, 3H), 4.00 (s, 18H), 3.09–3.28 (m, 48H), 2.58–2.76 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 165.6, 152.0, 144.6, 138.5, 137.7, 136.5, 131.1, 130.2, 126.3, 125.2, 124.3, 121.5, 91.4, 88.6, 71.6, 69.9, 67.1, 58.9, 52.5, 51.6, 36.1, 30.9.

*2.2.6. Triacid fluorophore (**1**)*

A mixture of **7** (50 mg, 0.035 mmol) in THF (8 mL) and methanol (8 mL) was added saturated KOH aqueous solution (0.5 mL) and the mixture was stirred at room temperature. After 24 h the solution was evaporated and the residue dissolved in water (30 mL). Ice was added to the aqueous layer which is acidified and the mixture kept in refrigerator. The product was filtered to afford **1** as a yellow solid (40 mg, 82%). ^{1}H NMR (CD_3CN, 400 MHz, ppm) δ 8.46 (d, J = 8.4 Hz, 3H), 8.04 (d, J = 8.4 Hz, 6H), 7.94 (s, 3H), 7.71 (d, J = 8.4 Hz, 9H), 3.01–3.22 (m, 48H), 2.72 (m, 12H), 2.60 (m, 6H). ^{13}C NMR (DMSO-d6, 100 MHz, ppm) δ 166.6, 152.3, 144.4, 138.5, 137.1, 131.5, 131.4, 130.9, 129.7, 126.6, 126.2, 124.9, 120.6, 92.4, 89.5, 70.8, 69.1, 66.4, 57.8, 51.5, 35.3. HRMS (EI) Calcd. for $C_{84}H_{90}O_{18}$ $(M + K)^+$ 1425.5764, found 1425.5757.

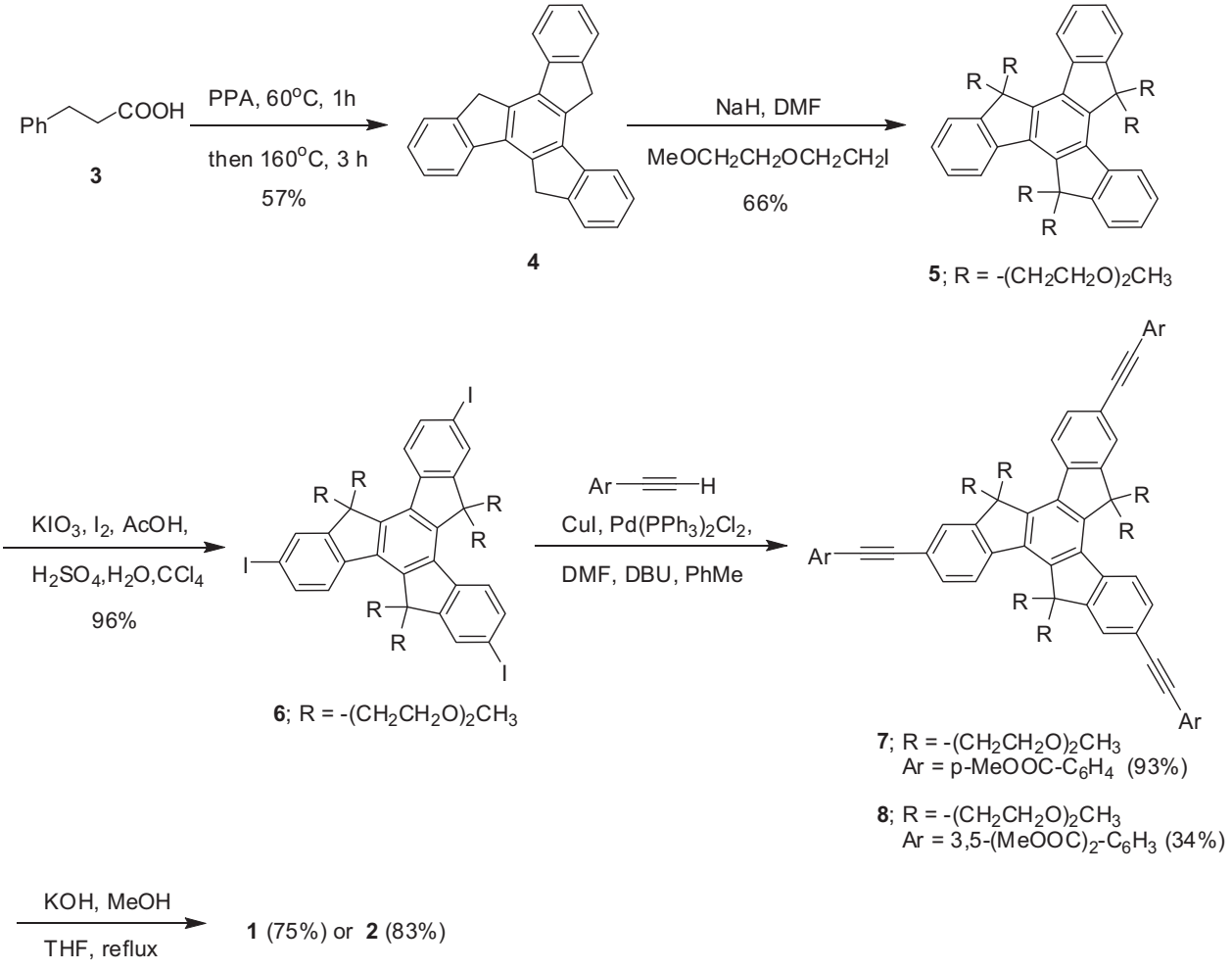
*2.2.7. Hexaacid fluorophore (**2**)*

A mixture of **8** hexaester (30 mg, 0.018 mmol) in THF (5 mL) and methanol (5 mL) was added saturated KOH aqueous solution (0.5 mL) and the mixture was stirred at room temperature. After 24 h the solution was evaporated and the residue dissolved in water (30 mL). Ice was added to the aqueous layer which is acidified and the mixture kept in refrigerator. The product was filtered to afford **2** as a yellow solid (21 mg, 75%). ^{1}H NMR (DMSO-d6, 400 MHz, ppm) δ 8.46 (s, 3H), 8.42 (d, J = 7.8 Hz, 3H), 8.31 (s, 6H), 8.14 (s, 3H), 7.77 (d, J = 7.8, 3H), 2.92–3.12 (m, 48H), 2.59 (m, 18H). ^{13}C NMR (DMSO-d6, 100 MHz, ppm) δ 165.9, 152.3, 144.4, 138.5, 137.1, 135.4, 132.3, 130.9, 129.7, 126.4, 124.9, 123.3, 120.5, 91.3, 88.4, 70.8, 69.1, 66.4, 57.8, 51.5, 35.3. HRMS (EI) Calcd. for $C_{87}H_{90}O_{24}$ $(M + K)^+$ 1557.5459, found 1557.5489.

3. Results and discussion

*3.1. Synthesis of anionic fluorophores **1**–**2***

Our synthesis began with a dehydration-trimerization of the commerically available hydrocinnamic acid (**3**) using a procedure reported by Yuan et al. [22] Scheme 1. Hexa-alkylation at three



Scheme 1. Synthesis of fluorophore **1** and **2**.

methylene units of truxene (**4**) was found very challenging. Various combinations of bases, solvents, and electrophiles such as 2-(2′-methoxy)ethoxyethyl tosylate or mesylate have been tested, most of which yielded mixtures of partially alkylated products. After several variations, it was found that the use of NaH and 2-(2′-methoxy)ethoxyethyl iodide in DMF could cleanly afford the hexa-alkylated truxene core **5** in 66% yield after a simple chromatography on silica gel column. Iodination of **5** using KIO_3 and I_2 gave rise to the 2,7,12-triiodo **6** as a single regiosiomer in excellent yield of 96%. The Sonogashira coupling of **6** with aryl acetylene **7** or **8** followed by the hydrolysis of ester groups afforded ionizable tri- and hexa-carboxylic acid (**1** and **2**), respectively.

3.2. Photophysical properties of fluorophores *1–2*

The electronic absorption spectra of **1** and **2** were acquired from 1 μM solutions in phosphate buffer pH 8. The absorption peak of both compounds displayed a typical vibrational progression pattern of truxene (Fig. 2). Extensions of the conjugated system caused longer absorption wavelengths in **1** and **2** compared to the starting truxene. The slightly longer wavelength of absorption of **1** suggested that the substitution of −COOH groups at the *para*-positions could cause a slightly larger π-ststem. The emission peak of **1** and **2** were at 402 and 400 nm in 10 mM phosphate buffer pH 8.0 with high quantum yields of 46 and 63%, respectively (Table 1). The larger overlapping between the absorption and emission spectral of **1** could cause the lower quantum yield, presumably due to the re-absorption of the emitted photon by molecules at the ground state [25].

3.3. Effect of pH on fluorescent intensities

The pH-dependent fluorescence studies of **1** and **2** were conducted in phosphate buffer at pH range of 2–10 (Fig. 3). At pH below 3, both **1** and **2** showed no fluorescence, which could be attributed to their poor solubility as a result of low degree of ionization of the carboxylic acid groups under highly acidic condition. The fluorescent intensities reach their maximum plateaus at pH 6. While **1** exhibited one-step fluorescent intensity increase starting around pH 4, compound **2** however displayed two-step increments taking off at pH 3 and 4, respectively. The two-step increase of the fluorescent intensity corresponded well with the two ionization processes of the dicarboxylic acid groups on each branch of the structure of **2**.

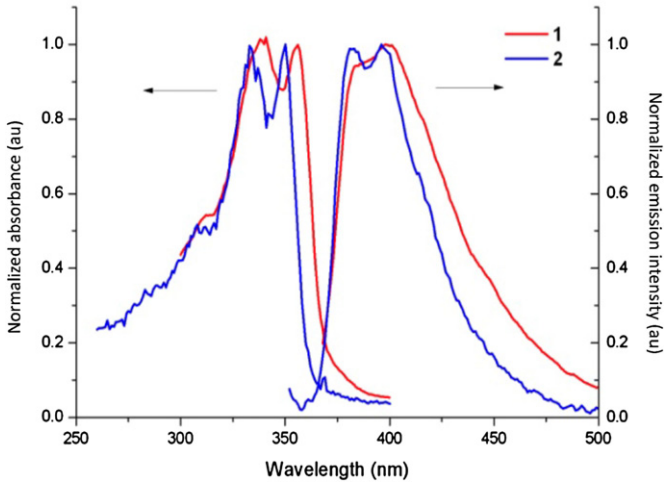


Fig. 2. Normalized absorption and emission spectra of **1** and **2** (1 μM) in phosphate buffer pH 8.

Table 1
Photophysical properties of **1** and **2**.

Cmpd.	Absorption		Emission	
	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	Φ_F[a]
Truxene[b]	275	–	346	–
	298	–	359	–
1	336	47700	387	0.46
	356	44400	402	
2	332	39300	383	0.63
	350	40300	400	

[a] 2-aminopyridine in 0.1 M H_2SO_4 ($\Phi_F = 0.60$) was the reference.
[b] dissolved in 9:1 DMSO:H_2O.

3.4. Fluorescent responses by proteins

Several literature reports on fluorescent protein sensor arrays [26–28] and the presence of anionic peripheral groups inspired us to use **1** and **2** as fluorescent sensors for proteins. The solution of fluorophores (1 μM) was tested with 8 protein solutions (A_{280} = 0.05) with a broad range of pI values and molecular weights. The selected proteins included metalloproteins such as myoglobin (Myo, pI = 7.2, 17.0 kDa), cytochrome c (CytC, pI = 10.7, 12.3 kDa) and carbonic anhydrase (CA, pI = 5.9, 29.0 kDa) and non-metalloproteins such as bovine serum albumin (BSA, pI = 4.8, 66.3 kDa), histone (His, pI = 10.8, 21.5 kDa), human serum albumin (HSA, pI = 5.2, 69.4 kDa), lysozyme (Lys, pI = 11.0, 14.4 kDa), and papain (Pap, pI = 9.6, 23.0 kDa). The dependence of fluorescence responses on the nature of proteins is illustrated in Fig. 4. It was evident that both compounds exhibited selective fluorescence quenching by metalloproteins containing porphyrin unit – CytC and Myo. In order to evaluate the quenching efficiency of the two proteins, Stern–Volmer plots were constructed by varying the protein concentration and monitoring the fluorescent signal of the fluorophores. In the presence of CytC, the K_{SV} of 2.53×10^5 M^{-1} and 2.01×10^5 M^{-1} were obtained for **1** and **2**, respectively (Fig. 5a,b). For the detection of Myo, the K_{SV} was 1.59×10^5 M^{-1} for **1** and 1.47×10^5 M^{-1} for **2** (Fig. 5c,d). The fact that CytC and Myo exhibited fluorescence quenching suggested that these responses might cause by the electron transfer process between metal-porphyrin moiety in the proteins and the fluorophore. This hypothesis is currently under investigation.

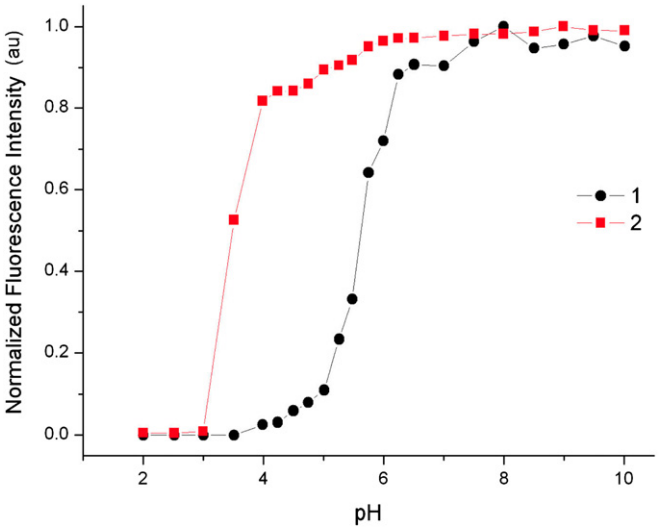


Fig. 3. pH dependence of the fluorescence intensity for **1** and **2** measured at room temperature. Excitation wavelength is 356 nm for **1** and 350 nm for **2**, observed emission wavelength is 400 nm for both compounds.

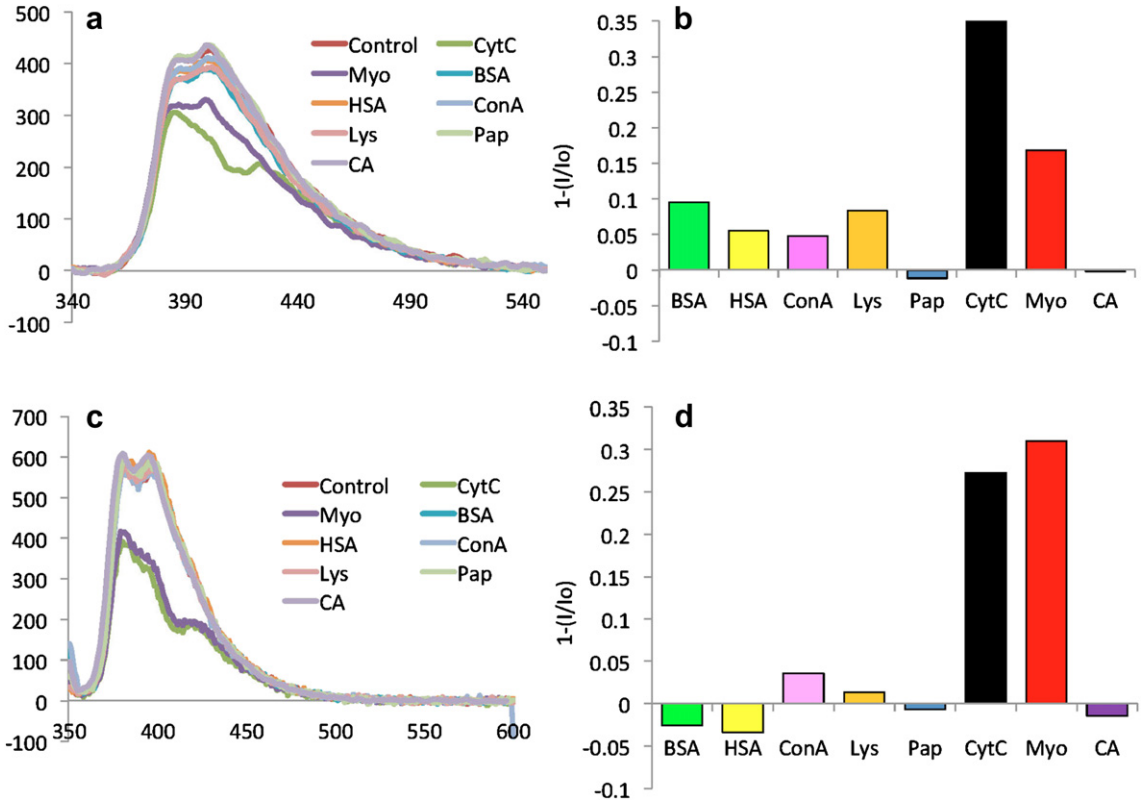


Fig. 4. (a) and (b) Fluorescence responses of 1; (c) and (d) fluorescence responses of 2 (1 μM) to various protein solution ($A_{280} = 0.05$) in phosphate buffer saline (10 mM, pH 7.4). Excitation wavelength is 356 nm for **1** and 350 nm for **2**, observed emission wavelength is 400 nm for both compounds.

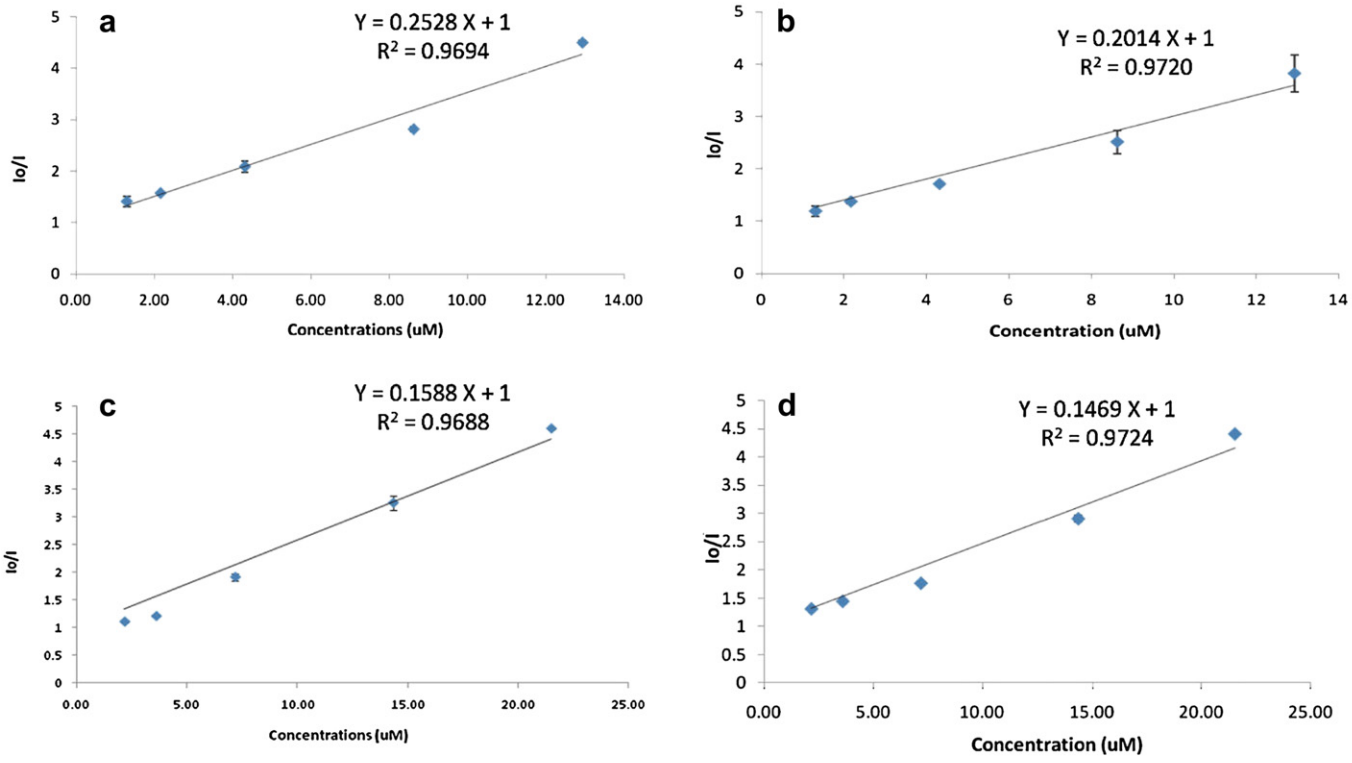


Fig. 5. (a) and (b) Stern–Volmer plots for fluorescence quenching of **1** and **2** by Cytochrome C, (c) and (d) Stern–Volmer plots for fluorescence quenching of **1** and **2** by Myoglobin.

4. Conclusion

In conclusion, we have accomplished the synthesis of two new anionic fluorophores from truxene. To the best of our knowledge, they are the first examples of water-soluble truxene derivatives in the literatures. With six 2-(2′-methoxy)ethoxyethyl groups decorated at the methylene units and three or six carboxylic acid peripheries, both compounds possessed excellent solubilities in aqueous media. They also exhibited outstanding emission quantum efficiencies typical for truxene derivatives which indicated a low degree of aggregation. Both fluorophores showed a selective fluorescent quenching by cytochrome C and myoglobin. Further examinations on mechanism of fluorescent quenching by these porphyrin-containing metalloproteins are currently in progress.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2011.10.009.

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