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New fluoride fluorescent chemosensors based on perylene derivatives linked by urea

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Abstract

Two dimers, based on perylene derivatives linked by urea, were synthesized; both dimers are in linear conformations. Fluorescence lifetimes and fluorescent properties of the dimers were investigated. They show fluorescence quenching in the presence of fluoride ion. The binding constants were calculated by the change of fluorescence, and the values were high (of the order of $\sim 10^5\ M^{-1}$).

Keywords: Synthesis; Perylene; Chemosensor; Fluorescence

Anions play an important role in numerous kinds of chemical and biological processes, and considerable efforts have been devoted to design the receptors or sensors that have the ability to selectively bind and sense anions [1]. The construction of anion chemosensor may couple at least two units, the binding site and the signaling subunit, which may be covalently or non-covalently linked [2,3]. Following the coordination of the binding site to a certain anion, some spectroscopic characteristics (color, fluorescence or electrochemistry) change. Of these spectroscopic changes, fluorescent chemosensor is particularly attractive on account of its simplicity and high sensitivity. However, the number of fluorescent sensors for fluoride anions is quite limited in spite of their importance in dental care and the treatment of osteoporosis [4–9]. In this study, we synthesized fluoride selective fluorescent chemosensor **TM1** and **TM2** (Fig. 1, Scheme 1), based on a urea derivative, which shows red fluorescence quenching in the presence of fluoride ions.

A urea moiety was chosen for binding site because it is a powerful hydrogen bond donor [10] that can bind anions solely via hydrogen bonding. Jagessar and Burns [11] and Jagessar et al. [12] reported that (*cis*)-5,10,15,20-tetrakis[2-(aryl urea)phenyl]-porphyrin containing different substitutions is selective for chloride over nitrate and dihydrogen phosphate anions in DMSO-d_6 solution, forming a 1:1 stoichiometry. More recently, Kim and co workers [9] reported that a naphthalene urea derivative showed a unique fluorescent and absorption peak in the presence of fluoride ions and the association constant for F^- was $14\,200\ M^{-1}$. Perylene dyes are chosen as fluorescence-monitoring units due to their outstanding chemical, thermal and photochemical stability [13] as well as their near-unit fluorescence quantum yield with red color emission [14] which avoids the noise from biological blue fluorescent background.

The synthesis of **TM1** and **TM2** began from amine **4a** and **4b**, which was reacted in $CHCl_3$ with 1.3 equiv. of triphosgene to provide **TM1** and **TM2** in $\sim$48% yield.

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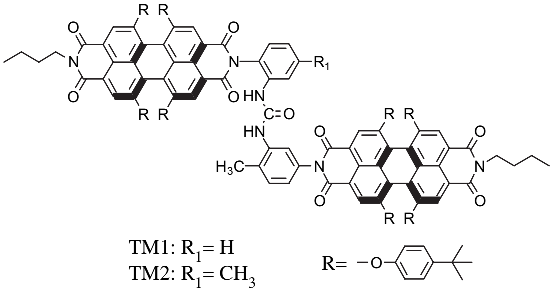
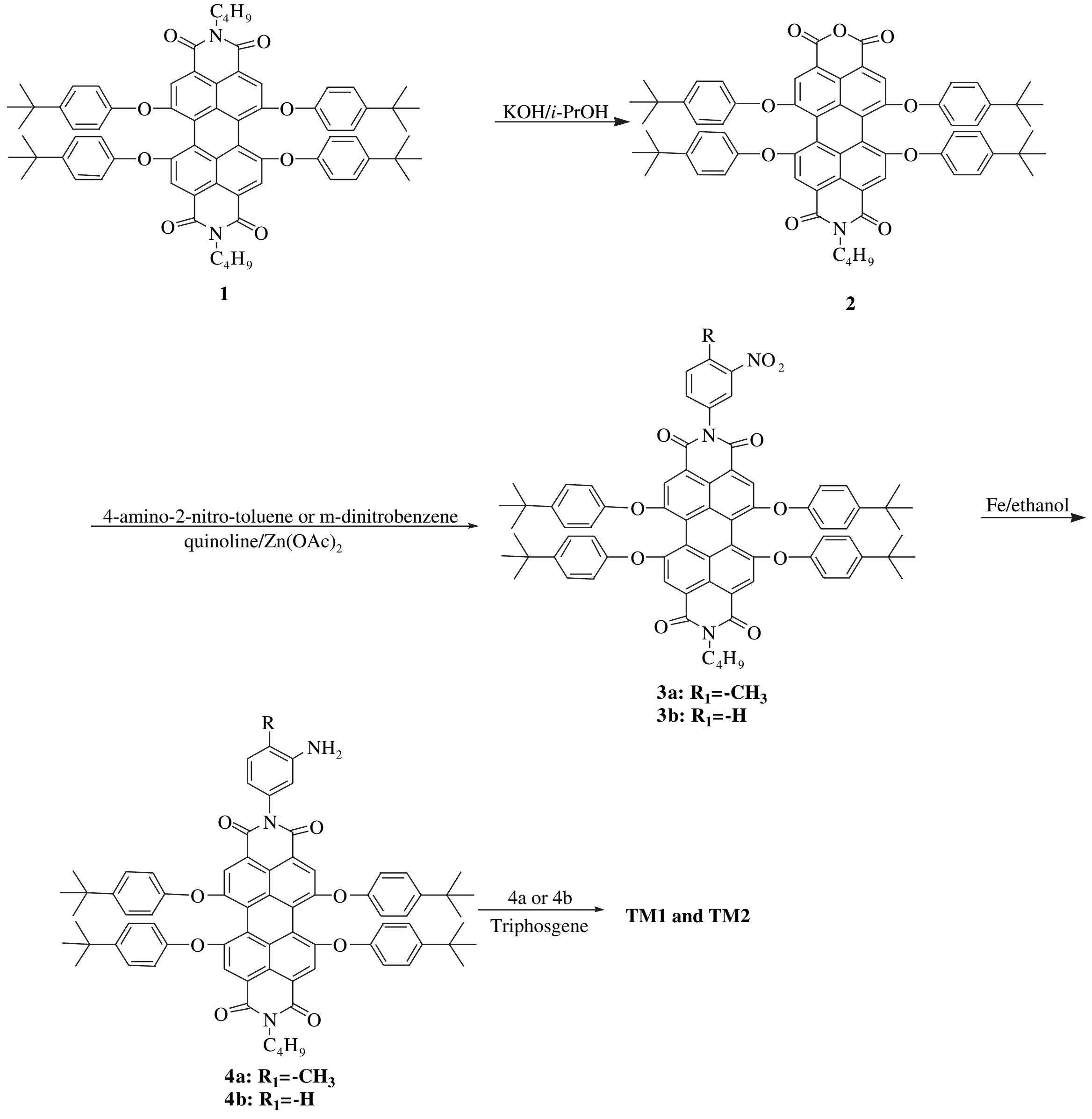


Fig. 1. The molecular structures of two dimers.

The effect of anions (as tetrabutylammonium salts) on the fluorescence spectra of **TM1** and **TM2** was investigated in THF, and the results show that the presence of F$^-$ resulted in a fluorescence decrease at 450, 540 and 580 nm while Cl$^-$, Br$^-$ and I$^-$ have almost no influence on the fluorescence.

1. Experimental

^{1}H NMR spectra were obtained using a Brücker AM 500 spectrometer. Mass spectra (MS) were carried on a MA1212 instrument. UV–vis spectra were performed on a Varian Cray500 spectrophotometer. Fluorescence spectra were recorded on a Varian Cray Eclipse Fluorescence Spectrophotometer. The fluorescence lifetime study was performed by an Edinburgh FL 900 single-photon counting system with a hydrogen-filled flash lamp or a nitrogen lamp as the excitation source. Data were analyzed using a nonlinear least-square fitting



Scheme 1. Synthesis route of the two dimers.

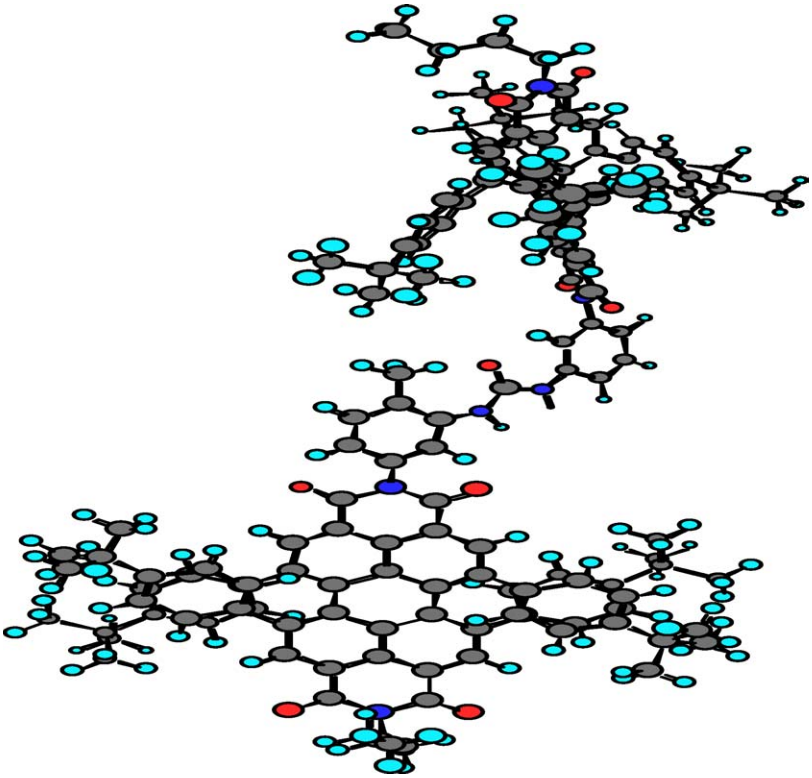


Fig. 2. Energy-minimized molecular modeling of **TM1**.

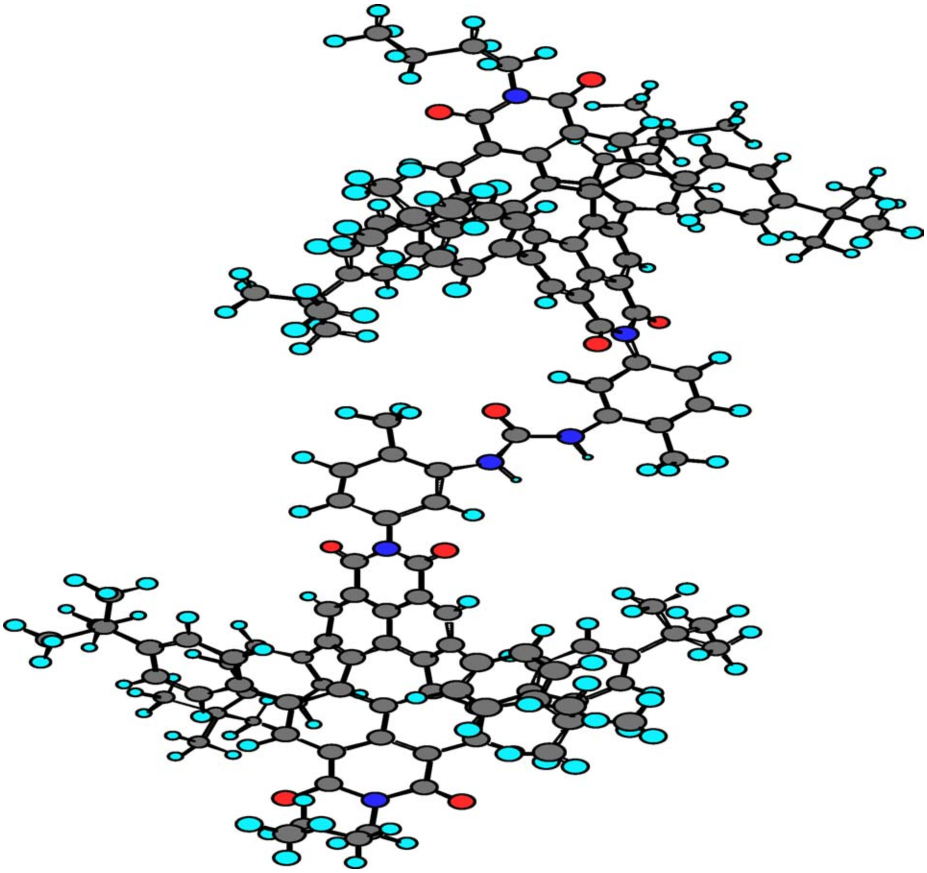


Fig. 3. Energy-minimized molecular modeling of **TM2**.

Table 1
The calculated steric energies of the dimers for different conformations

Compounds	Folded conformation (kcal/mol)	Linear conformation (kcal/mol)
TM1	784.8498	43.2105
TM2	760.0201	44.1105

program with deconvolution of the exciting pulse being ~200 ps [15].

1.1. N′-tetra-butyl-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4-anhydride-9,10-imide (2) [16]

Partial purification of *N*,*N*′-dibutyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisimide (3.3 g, 3.0 mmol) with KOH (75 g, 134 mmol) in isopropyl alcohol (500 mL) and H_2O (50 mL) under argon by stirring at reflux for 15 h, followed by acidic workup, and thorough washing and drying, yielded a mixture (2.5 g) of perylene bisanhydride and perylene mono butylimide **2** in a ratio of about 6:4. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.22 (d, $J = 2.47$ Hz, 4H), 7.22 (d, $J = 14.34$ Hz, 8H), 6.83 (d, $J = 14.34$ Hz, 8H), 4.10 (t, $J = 7.53$ Hz, 7.51 Hz, 2H), 1.65 (m, 2H), 1.35 (m, 2H), 1.29 (s, 36H), 0.84 (t, $J = 6.68$ Hz, 7.09 Hz, 3H).

1.2. N-(4-methyl-3-nitrophenyl)-N′-butyl-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisimide (3a)

Perylene mono butylimide **2** (1.5 g, 1.4 mmol), 4-amino-2-nitro-toluene (3.2 g, 23.2 mmol), and zinc(II) acetate (0.15 g, 0.9 mmol) were stirred under argon at 180 °C for 16 h in quinoline (40 mL). HCl (2 N, 150 mL) was added, and the precipitate was collected, washed with water and methanol, and dried. Column chromatography (toluene) afforded **3a** (1.21 g, 72% yield). M.p. > 300 °C.

1.3. N-(3-nitrophenyl)-N′-butyl-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisimide (3b)

Perylene mono butylimide **2** (1.5 g, 1.4 mmol), 3-nitro-toluene (3.2 g, 21.0 mmol) and zinc(II) acetate (0.15 g, 0.9 mmol) were allowed to react and worked up in the same way as described for **3a** to give **3b** (1.14 g, 75% yield). M.p. > 300 °C.

Table 2
The fluorescence lifetimes of the dimers in solvents (excited at 380 nm; probed at 520 nm)

Compounds	In $CHCl_3$ (ns)	In CH_2Cl_2 (ns)	In THF (ns)	In acetonitrile (ns)	In cyclohexane (ns)
TM1	5.988	6.166	4.911	3.614	6.133
TM2	6.045	5.756	4.918	3.435	6.408

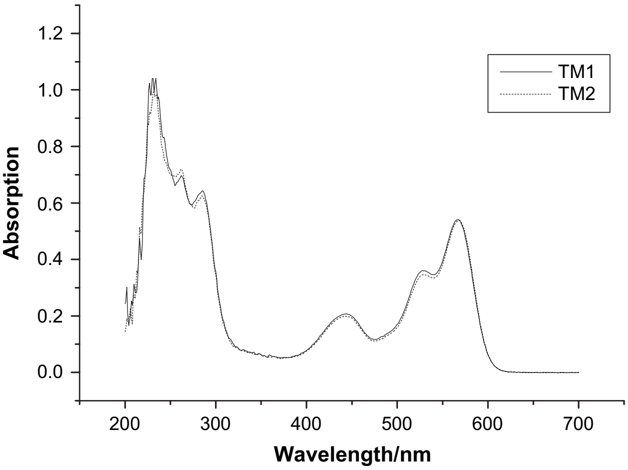


Fig. 4. Absorption spectra of **TM1** and **TM2** in THF (10^{-5} mol/L).

1.4. N-(4-methyl-3-aminophenyl)-N′-butyl-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisimide (4a)

A mixture of compound **3a** (0.4 g, 0.34 mmol), 1.8 g (32.1 mmol) iron powder, 200 mL ethanol, 150 mL acetone and 10 mL water was heated to reflux. Two milliliters of 10% HCl was added under N_2 and the mixture refluxed for another 3 h. Then the mixture was filtered with hot and the solvent was removed by rota evaporation. Purification was carried out by column chromatography on a silica gel with CH_2Cl_2 as eluent, affording 0.18 g of the title compound (48% yield). M.p. > 300 °C; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.22 (d, $J = 16.82$ Hz, 4H), 7.27 (m, 9H), 7.15

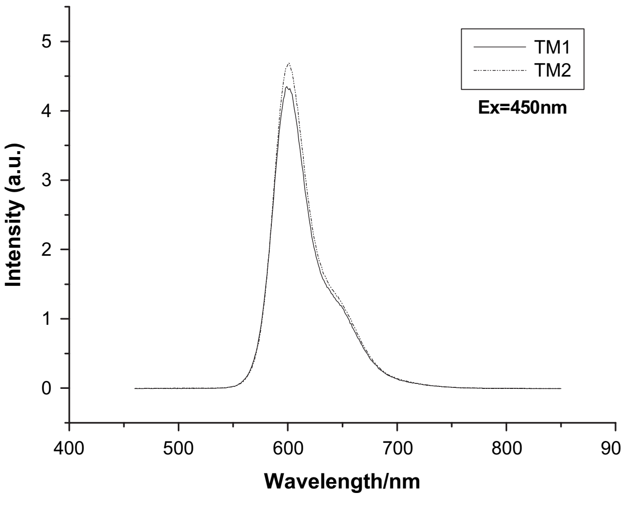


Fig. 5. Fluorescence spectra of **TM1** and **TM2** in THF (10^{-5} mol/L).

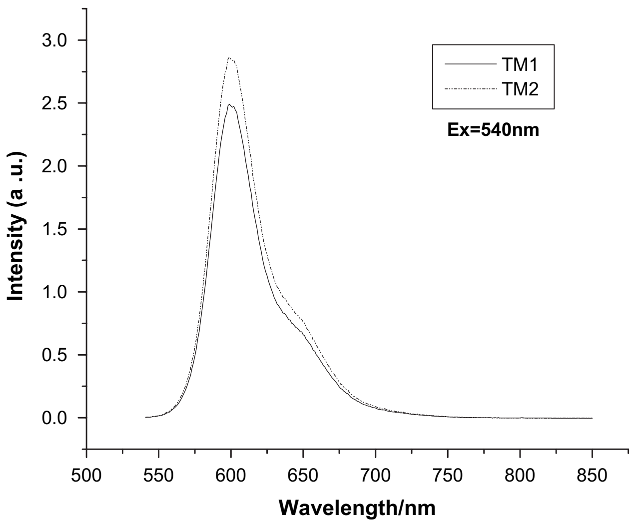


Fig. 6. Fluorescence spectra of **TM1** and **TM2** in THF (10^{-5} mol/L).

(d, $J = 8.1$ Hz, 1H), 6.84 (m, 8H), 6.62 (s, 1H), 4.12 (t, $J = 7.38$ Hz, 7.51 Hz, 2H), 2.21 (s, 3H), 1.65 (m, 2H), 1.35 (m, 2H), 1.28 (s, 18H), 1.26 (s, 18H), 0.95 (t, $J = 7.33$ Hz, 7.37 Hz, 3H).

*1.5. N-(3-aminophenyl)-N′-butyl-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisimide (**4b**)*

The mixture of compound **3a** (0.4 g, 0.34 mmol), 1.8 g (32.1 mmol) iron powder, 200 mL ethanol, 150 mL acetone and 10 mL water was allowed to react and worked up in the same way as described for **4a** to give **4b** (0.19 g, 50% yield). M.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.20 (d, $J = 16.80$ Hz, 4H), 7.24 (m, 9H), 6.83 (m, 8H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 7.2$ Hz, 1H), 6.56 (s, 1H), 4.13 (t, $J = 7.38$ Hz, 7.51 Hz, 2H), 1.66 (m, 2H), 1.36 (m, 2H), 1.28 (s, 18H), 1.25 (s, 18H), 0.96 (t, $J = 7.45$ Hz, 7.50 Hz, 3H).

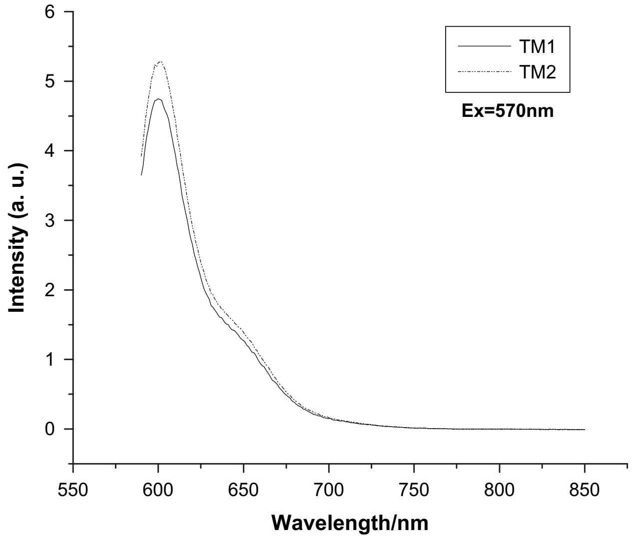


Fig. 7. Fluorescence spectra of **TM1** and **TM2** in THF (10^{-5} mol/L).

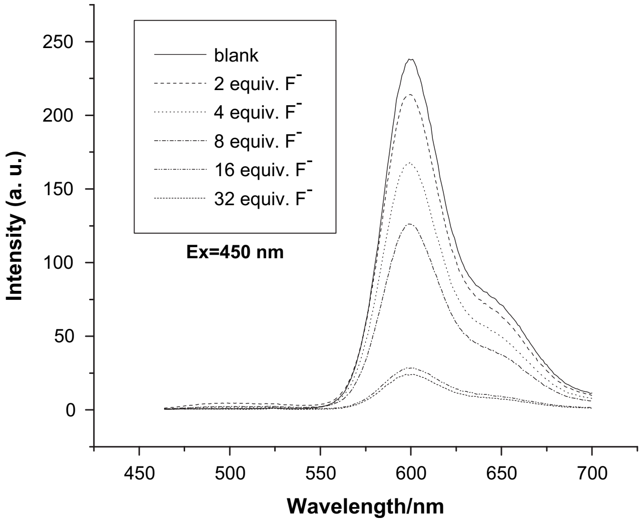


Fig. 8. Fluorescence titration spectra of **TM1** with n-$Bu_4N^+F^-$ in THF.

*1.6. Perylene dimer **TM1**[17]*

To a stirred solution of **4a** (0.3 g, 0.26 mmol) and Et_3N (0.20 g, 2.0 mmol) in $CHCl_3$ (10 mL) triphosgene (0.1 g, 0.35 mmol) was added under N_2. The reaction mixture was stirred at room temperature for 1 h, after which **4b** (0.3 g, 0.27 mmol) was added and refluxed for 12 h. The solvent was removed by rota evaporation, and purification was carried out by column chromatography on a silica gel with CH_2Cl_2 and EtOAc (v/v = 75:1) as eluent, affording 0.29 g of **TM1** (49% yield).

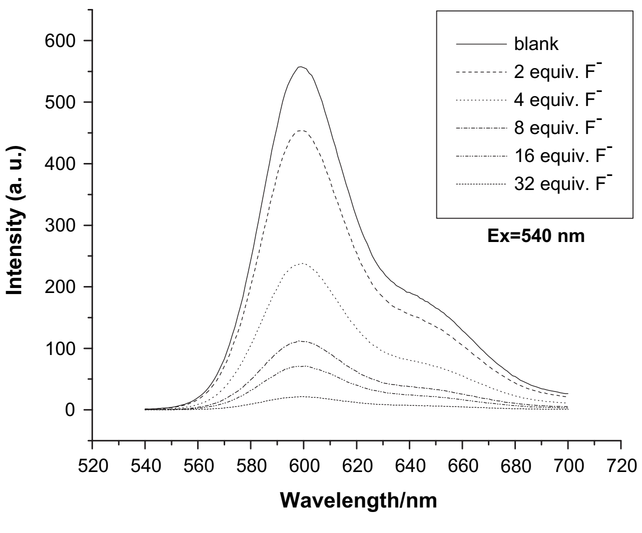


Fig. 9. Fluorescence titration spectra of **TM1** with n-$Bu_4N^+F^-$ in THF.

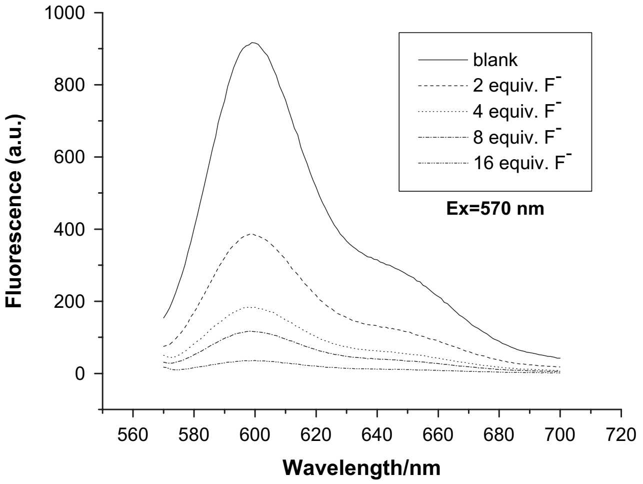


Fig. 10. Fluorescence titration spectra of **TM1** with n-$Bu_4N^+F^-$ in THF.

M.p. > 300 °C ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.23 (s, 4H), 8.20 (s, 2H), 8.18 (s, 2H), 7.79 (s, 2H), 7.21 (m, 19H), 6.80 (m, 18H), 4.23 (t, J = 7.26 Hz, 4H), 2.05 (s, 3H), 1.78 (m, 4H), 1.45 (m, 4H), 1.24 (s, 36H), 1.22 (s, 36H), 0.90 (t, J = 7.32 Hz, 6H).

1.7. Perylene dimer **TM2**[17]

The mixture of **4a** (0.6 g, 0.52 mmol), Et_3N (0.20 g, 2.0 mmol) and triphosgene (0.1 g, 0.35 mmol) was allowed to react and worked up in the same way as described for **TM1** to give **TM2** (0.29 g, 48% yield). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.23 (s, 4H), 8.19 (s, 4H), 7.80 (s, 2H), 7.20 (m, 18H), 6.83 (m, 18H), 4.13 (t, J = 7.23 Hz, 4H), 2.08 (s, 6H), 1.65 (m, 4H), 1.40 (m, 4H), 1.25 (s, 36H), 1.23 (s, 36H), 0.94 (t, J = 7.35 Hz, 6H).

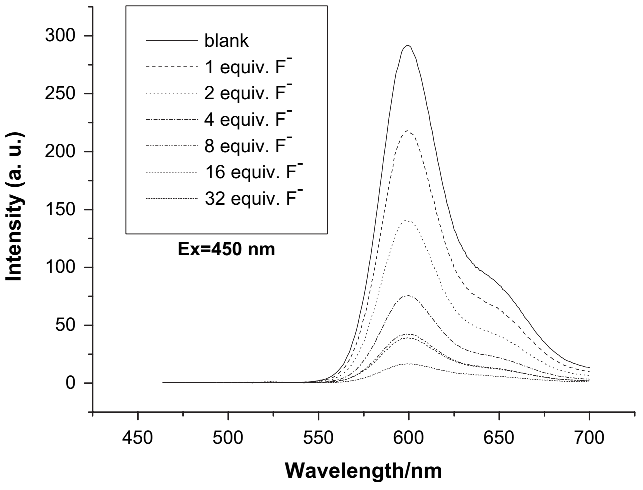


Fig. 11. Fluorescence titration spectra of **TM2** with n-$Bu_4N^+F^-$ in THF.

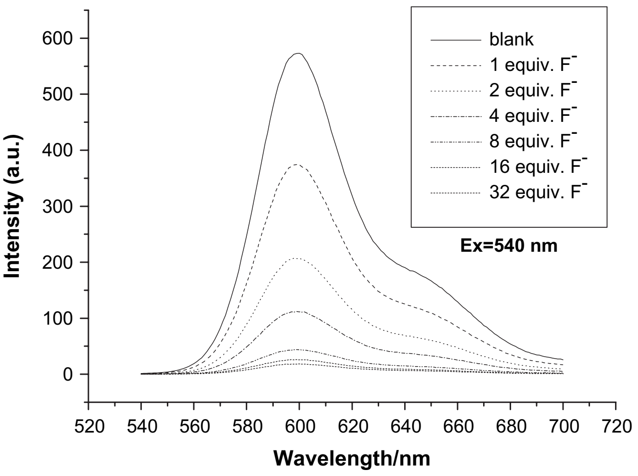


Fig. 12. Fluorescence titration spectra of **TM2** with n-$Bu_4N^+F^-$ in THF.

2. Results and discussion

2.1. Geometries of the dimers

There may exist two conformations in the dimers, the folded and the linear as shown in Figs. 2 and 3. Using MM2, we can easily calculate that the total steric energy of **TM1** for folded configuration which is high up to 784.8498 kcal/mol, while that for the linear confirmation is 43.2105 kcal/mol, as shown in Table 1. Then we can conclude that dimer **TM1** is positioned in a linear geometry. Similarly, comparing 760.0201 kcal/mol for the folded orientation with the value of 44.1105 kcal/mol for the linear orientation, dimer **TM2** is also in a linear geometry.

In addition, we also determined the lifetimes of the dimers, the results of which are listed in Table 2. All the lifetimes of the two dimers in the same solutions have almost no difference (the system error is 0.3 ns); these

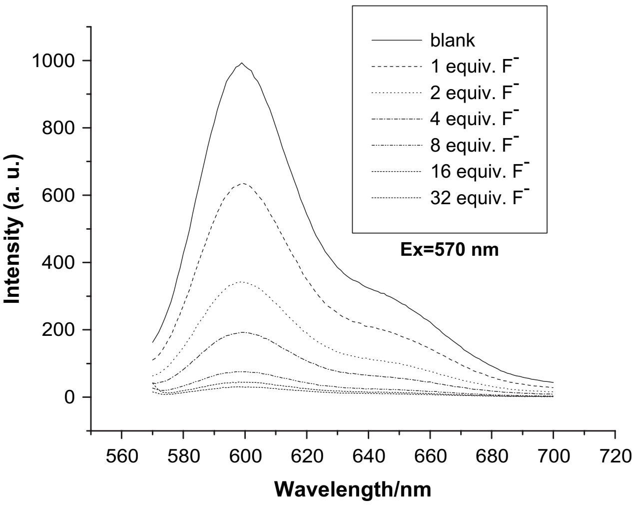


Fig. 13. Fluorescence titration spectra of **TM2** with n-$Bu_4N^+F^-$ in THF.

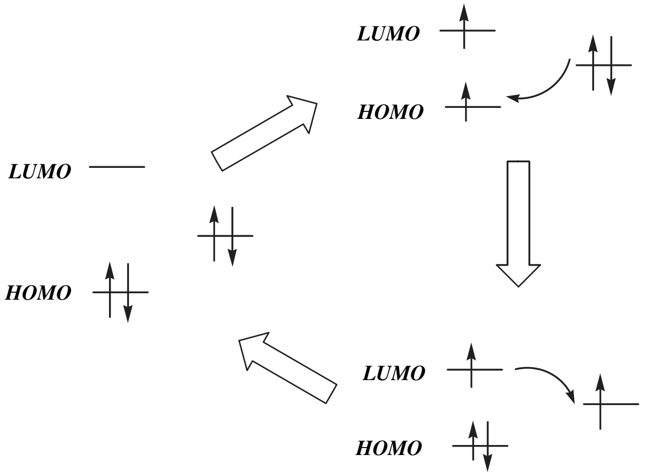


Fig. 14. Photon-induced electron transfer (PET) process with the participation of HOMO and LUMO of the fluorophore and an external molecular orbital.

results prove likewise that the dimers are in the same conformations.

2.2. Fluorescent sensor to F^- ion

The UV–vis absorption spectra of **TM1** and **TM2** are shown in Fig. 4, and fluorescence spectra of the same are shown in Figs. 5–7. Both absorption and fluorescence spectra of **TM1** and **TM2** in the same solution are almost same indicating that the two dimers are in identical configurations. As shown in Figs. 8–13, the presence of F^- results in the fluorescence quenching of **TM1** and **TM2**, and the quenching efficiency increases along with the increase in concentration of F^-. In particular, upon addition of F^- to the solution of the dimers in a 32-fold excess, the fluorescence of perylene almost quenched completely. However, when Br^-, Cl^- and I^- were added in 32-fold excess, nearly no obvious spectral change was observed. These results suggested that the dimers have a higher selectivity for F^- compared to the other halide anions. The selectivity for F^- can be attributed to Brønsted basicity of the receptor. The F^- anions have the strongest basicity, and also exhibit the most effective hydrogen binding interaction with the binding site, urea group.

F^- coordination to the binding site of the dimers results in a quenching of the perylene emission. This may be due to the fact that upon F^- coordination, the reduction potential of the urea increases causing PET to become competitively more viable. Fluorescence quenching occurs because the transition from the excited state to ground state takes place following a non-radiative path, as shown in Fig. 14 [18].

When the electron of the fluorophore in the HOMO orbit was excited, it goes to LUMO orbit and releases the excess energy, such as fluorescence. The nitrogen atom of the urea group has an occupied orbit, and when it coordinates to the F^-, this orbit may be located between the LUMO and HOMO of the fluorophore, perylene. When the electron of the fluorophore is excited, a PET process from this occupied orbit to HOMO takes place. Further, the electron gets transferred from LUMO to the orbit, and finally it retrieves to the ground state. So the fluorescence is quenched via this non-radiative path.

The binding constant can be calculated by the change of fluorescence [19], as shown in the equation below:

$$F_0/F = 1 + K_{11}[L]$$

where F_0 and F are the fluorescence intensities in the absence and presence of the anions, respectively, and $[L]$ is the concentration of the anions. The association constants were calculated to be $1.03 \times 10^5\ M^{-1}$ for **TM1** and $1.017 \times 10^5\ M^{-1}$ for **TM2**.

In summary, two new fluoride chemosensors, perylene derivative dimers linked by urea, have been synthesized. Both adopt linear configurations, and their absorption, fluorescence spectra and fluorescence are almost identical. They show very sensitive fluorescence quenching in the presence of fluoride ion. The binding constants were calculated by the change of fluorescence, and the values were high (of the order of $\sim 10^5\ M^{-1}$). When Cl^-, Br^- and I^- anions were added, no obvious fluorescence changes were observed.

Acknowledgments

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