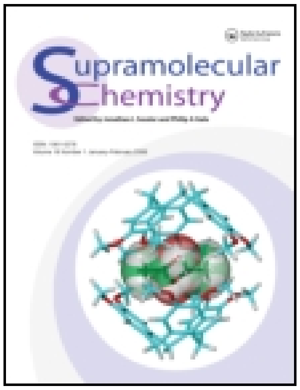


Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

An ion-responsive fluorescent compound based on NO-photoisomerisation styryl derivative linked to monoaza-15-crown-5

Jing Cao [a] [b] , Jun Xiang Feng [a] , Yong Xiang Wu [a] , Xue Qun Pei [a] , Jiao Jiao Yan [a] , Yang Liu [a] , Wen Jie Qin [a] & Xiao Bin Zhang [a]

[a] College of Chemistry, Xiangtan University, Xiangtan, Hunan, 411105, P.R. China

[b] Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan, Hunan, 411105, P.R. China

To cite this article: Jing Cao, Jun Xiang Feng, Yong Xiang Wu, Xue Qun Pei, Jiao Jiao Yan, Yang Liu, Wen Jie Qin & Xiao Bin Zhang (2011): An ion-responsive fluorescent compound based on NO-photoisomerisation styryl derivative linked to monoaza-15-crown-5, Supramolecular Chemistry, 23:05, 407-410

To link to this article: http://dx.doi.org/10.1080/10610278.2010.532215

Supramolecular Chemistry
Vol. 23, No. 5, May 2011, 407–410

An ion-responsive fluorescent compound based on NO-photoisomerisation styryl derivative linked to monoaza-15-crown-5

Jing Cao[ab]*, Jun Xiang Feng[a], Yong Xiang Wu[a], Xue Qun Pei[a], Jiao Jiao Yan[a], Yang Liu[a],
Wen Jie Qin[a] and Xiao Bin Zhang[a]

[a]*College of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, P.R. China;* [b]*Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, P.R. China*

(*Received 1 May 2010; final version received 10 October 2010*)

A novel 15-aza-5-crown ether linked to styryl chemosensory 13-(4-((9*H*-fluoren-9-ylidene)methyl)-2-nitrophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane was designed and synthesised, it would not occur during photoisomerisation under radiation of light but shows special capability of selectively recognising for Sr^{2+}.

Keywords: 15-aza-5-crown ether; photoisomerisation; Sr^{2+}; fluorescent enhancement

Introduction

The photophysics and photochemistry of fluorophores linked to crown ethers or involved in complexing supramolecular structures are the areas of growing interest (*1–3*). Styryl compounds linked to azacrown ether yield molecular systems, where styryl moiety can provide the chromo- and fluorogenic properties. A lot of these styryl derivatives have been developed since several decades (Scheme 1), they were reported to have high fluorescence quantum efficiency and selectivity for the divalent alkaline earths, particularly Ca^{2+} (*4–10*). It is well known that stilbene would occur during *trans–cis* isomerisation under the radiation of light, because the torsion of double bond becomes easy in the excited state (*11*). Although introducing substituting groups on aromatic ring of stilbene may increase the torsional barrier of double bond, *trans–cis* photoisomerisation is still inevitable. Photophysical properties of fluorophore will be worst affected by the photoisomerisation in the styryl compounds containing azacrown group. This led us to synthesise a new styryl molecule 13-(4-((9*H*-fluoren-9-ylidene)methyl)-2-nitrophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (FMN-crown) with the aim at avoiding photoisomerisation. Herein, we report the preparation and spectroscopic study of this novel chemosensory.

Results and discussion

The synthetic route for fluorescent sensor FMN-crown is depicted in Scheme 2. Our synthesis began with 4-chlorobenzaldehyde, which produced 4-chloro-3-nitrobenzaldehye in the presence of HNO_3 and H_2SO_4. Pd-catalysed coupling reaction of **3** with aza-15-crown-5 in hexamethylphosphamide media afforded **2** (*12*), and then it reacted with triphenylphosphoniumfluorenylide to give the target product chemosensory FMN-crown (*13*).

In the case of a molecule containing a double bond, e.g. WXC═CYZ (W, X, Y, Z are substituting groups on the double bond), isomerisation will not exist where W═X or Y═Z (*14*); therefore, FMN-crown does not give isomers. The experiment demonstrates that FMN-crown is so stable in solution that repetitive absorption spectra show no change under ambient light for 4 weeks. Instead, the literature reported that some of the styryl compounds were linked to azacrown as given in Scheme 1, which show a partial conversion of the *trans* isomer into the *cis* isomer in a short period (*15*).

FMN-crown exhibits weak emission in acetonitrile as that of model compound **1a** in acetonitrile solution (Figure 1), which should be attributed to repulsion between benzene and fluorene. As we know, *trans*-stilbene shows strong emission in solution, whereas *cis*-stilbene shows almost no fluorescence emission, since a steric repulsion between two benzene moieties in the *cis*-stilbene molecule reduces conjugation of the system (*11*). A dihedral angle of the benzene and fluorene plane in model molecule **1a** was 41° through analysing on the Chem3D Ultra 10.0 program (Figure 2).

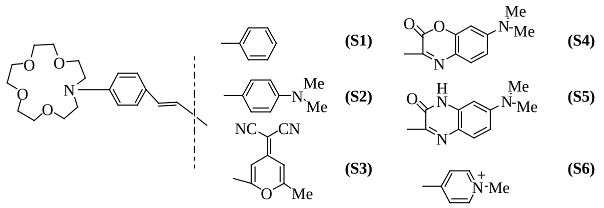
We have found that the FMN-crown strongly responds to certain metal cations. As shown in Figure 3, the 2.1-μM FMN-crown in acetonitrile undergoes an increase in quantum efficiency when complexed with some of the divalent cations. Consequently, the FMN-crown ether is found to be optically responsive to Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+}, which could also be observed

---

*Corresponding author. Email: caojing8088@xtu.edu.cn

ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610278.2010.532215
http://www.informaworld.com



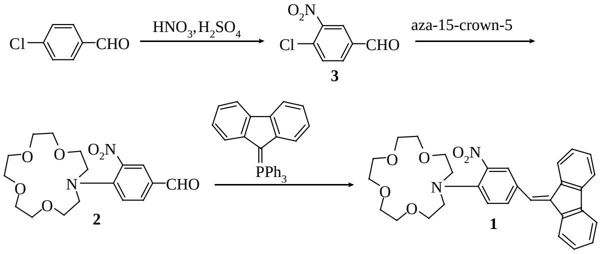
Scheme 1. Reported styryl compounds with aza-15-crown-5 group.

from the absorption spectra of FMN-crown (2.1×10^{-5} M) in acetonitrile at room temperature upon the addition of 50 equiv. of various metal cations (Figure 4).

Unlike some styryl compounds linked to azacrown, i.e. compound S3 in Scheme 1 (*8*), the emission of the FMN-crown is not quenched upon complexation. The observed variations in the FMN-crown emission spectrum with cations are believed to be due to the hindering process of photoinduced electron transfer between the aza group and fluorophore; complexation by cations reduces nitrogen atom donor character and thus hinders electron transfer (*16*).

Sr^{2+} is particularly reactive with the FMN-crown and causes a great increase in the fluorescence intensity. The other cations cause significantly smaller change than Sr^{2+}. Closely matching the crown cavity in size, Ca^{2+} has been previously shown to complex strongly with the aza-15-crown-5, binding with the lone pair of the macrocycle's aza group, creating the largest intensity change in the fluorescence emission peak of the alkaline earths (*17*). However, FMN-crown shows less sensitivity to Ca^{2+} and causes slightly change in the emission spectra. The nitro group on benzene near to crown ether is thought to have an effect on the complexation of azacrown with metal cations.

Fluorometric titrations were carried out by the addition of known quantities of metal cations to 2.1×10^{-6} M solution of free ligand. Titration of Sr^{2+} into acetonitrile solution of FMN-crown gave a concomitant enhancement of the fluorescence intensity (Figure 5). The monotonous dependence indicates a 1:1 stoichiometry within the concentration range investigated. The stability constant K_s was determined with linear least square analysis of $I_o/(I-I_o)$ vs. 1/[M] (*18*). The intercept/slope of the plot provided K_s with correlation coefficients better than 0.98, and K_s for Sr^{2+} is up to 1.6×10^3.



Scheme 2. Synthetic routes for chemosensory **1**.

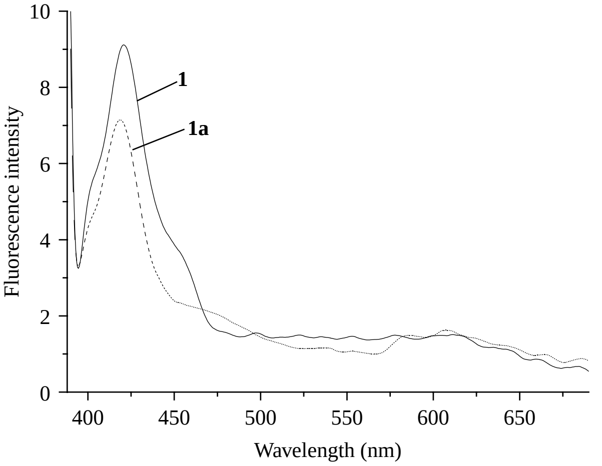


Figure 1. Fluorescence spectra of compound **1** and model compound **1a** (2.1×10^{-6} M) in acetonitrile at room temperature.

Conclusion

In conclusion, FMN-crown was designed to avoid photoisomerisation, by an appropriate introduction of the combination of fluorene group and carbon–carbon double bond. The novel crown ether exhibits high response ability for Sr^{2+}. Our further efforts will specifically elucidate the role of the nitro group in the photochemical behaviour of this stilbene-like molecule and develop new fluorescent chemosensory, molecular switches, photo devices and other photo-active materials.

Experimental

Reagents

The solvents and the reagents used in the synthesis of chemosensory **1** were purchased from Aladdin Reagent Company (Shanghai, China) and used without further purification. Analytical grade inorganic salts $NaClO_4$, $KClO_4$, $MgCl_2$, $CaCl_2$, $SrCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$,

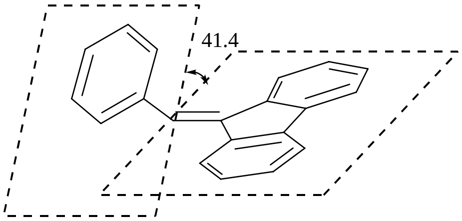


Figure 2. Dihedral angle of benzene and fluorene plane in model molecule **1a** through analysing on Chem3D Ultra 10.0 program.

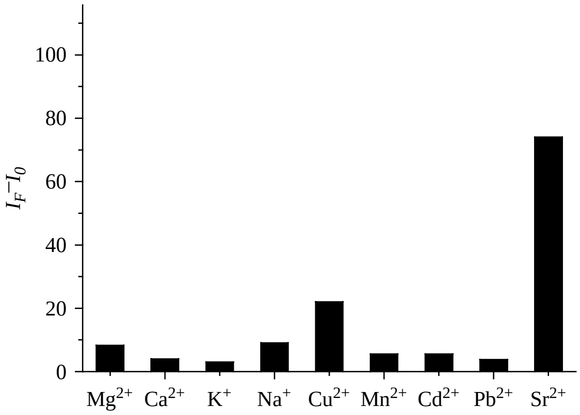


Figure 3. Fluorescence enhancement of compound **1** (2.1×10^{-6} M) in acetonitrile at room temperature upon addition of various metal cations; excitation at 378 nm; metal cations, 50 equiv. I_F is the fluorescence intensity of **1** with metal cations; I_0 is the fluorescence intensity of free **1**.

$MnSO_4$, $CdCl_2$ and $Pb(NO_3)_2$ were also purchased from this company.

Absorbance and fluorescence titrations

Absorption spectra were recorded on a Lambda 25 spectrophotometer under the control of a Pentium PC running the manufacturer-supplied software package. Fluorescence spectra were obtained on a Perkin-Elmer LS55 luminescence spectrometer with 10 nm excitation and emission slit widths, excitation at 378 nm. All solutions of fluorescent chemosensory **1** were prepared in spectroscopic grade acetonitrile without special efforts to exclude water or air. Fluorescence titrations were carried out with 10, 20, 50 and 100 µl metal ion aqueous solutions (2.1×10^{-6} M) to 5 ml acetonitrile solution of compound **1** (2.1×10^{-6} M), respectively.

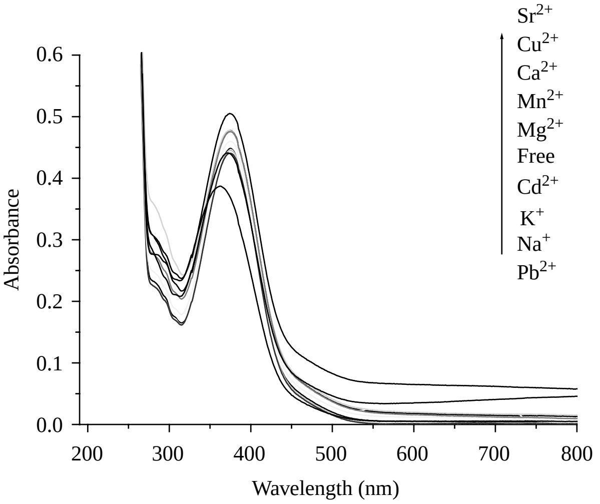


Figure 4. Absorption spectra of compound **1** (2.1×10^{-5} M) in acetonitrile at room temperature upon addition of 50 equiv. of various metal cations.

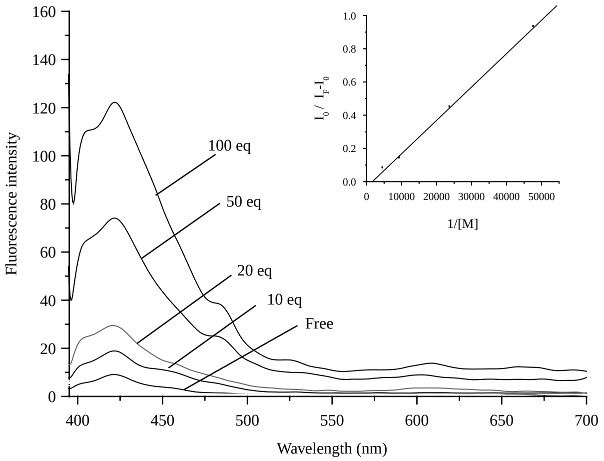


Figure 5. Titration profiles for fluorescence emission spectra of FMN-crown (2.1×10^{-6} M) with Sr^{2+} in acetonitrile.

Synthetic procedures and physical data

Process for preparation of 4-chloro-3-nitrobenzaldehyde (3)

4-Chlorobenzaldehyde (0.10 mol) was added for 20 min to a stirred mixture of HNO_3 (10.0 ml) and concentrated sulphuric acid (120 ml) in an ice bath. After 3 h of stirring at room temperature, the solution was poured onto ice (400 ml) and then precipitate was collected by filtration, washed with H_2O and dried on vacuum. The crude product was recrystallised from hexane to afford 4-chloro-3-nitrobenzaldehyde. Yield 45%, mp 61–62°C. ^1H NMR ($CDCl_3$) δ 10.06 (s, 1 H), 8.38 (s, 1 H), 8.05 (d, 1 H), 7.78 (d, 1 H). ^{13}C NMR ($CDCl_3$) δ 188.4, 135.4, 133.1, 133.0, 132.7, 126.3. Anal. Calcd for $C_7H_4ClNO_3$: C, 45.31; H, 2.17; N, 7.55. Found C, 45.38; H, 2.32; N, 7.75.

Process for preparation of 3-nitro-4-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)benzaldehyde (2)

To a stirred hexamethylphosphoramide solution of 4-chloro-3-nitrobenzaldehyde (0.2 g, 1.10 mmol), Pd $(CH_3COO)_2$ (10 mg) and *o*-phenanthroline (11 mg) were added, aza-15-crown-5 (0.24 g, 1.10 mmol) was slowly dropped in under N_2 protection. The reaction mixture was immersed in 80°C oil bath and stirred at this temperature for 24 h. After cooling to room temperature, the reaction mixture was diluted with 20 ml CH_2Cl_2, washed with water, dried over Na_2SO_4 and the solvent was removed on vacuum. The residue was purified by chromatography on silica gel, eluting with EtOAc–petroleum ether (1:1), to afford yellow oil product **2**. Yield 52%. ^1H NMR ($CDCl_3$) δ 9.89 (s, 1 H), 8.15 (s, 1 H), 7.88 (m, 1 H), 7.35 (m, 1 H), 3.75 (m, 4 H), 3.62 (m, 16 H). ^{13}C NMR ($CDCl_3$) δ 188.7, 148.2, 139.2, 132.3, 129.9, 126.5, 117.6, 71.1, 70.5, 70.3, 68.7, 53.4. Calcd for $C_{17}H_{24}N_2O_7$: C, 55.43; H, 6.57; N, 7.60. Found C, 55.48; H, 6.72; N, 7.67.

*Process for preparation of FMN-crown,**1***

To a solution of triphenylphosphoniumfluorenylide (0.188 g, 0.43 mmol) in 5 ml of chloroform compound **2** was added (0.160 g, 0.43 mmol). After heating the orange solution under reflux for 3 h, the solvent was evaporated on the steam bath. The residual oil was purified by chromatography on silica gel, eluting with EtOAc–petroleum ether (1:1), to afford orange oil product **1**. Yield 45%. ^{1}H NMR ($CDCl_3$) δ 7.71–7.94 (m, 12 H), 3.61–3.77 (m, 20 H). ^{13}C NMR ($CDCl_3$) δ 144.0, 141.7, 141.4, 139.4, 139.1, 136.7, 136.1, 133.9, 128.8, 128.3, 128.1, 127.1, 126.9, 126.8, 124.5, 124.0, 122.0, 120.2, 119.9, 119.6, 71.1, 70.6, 70.5, 69.4, 53.6. Calcd for $C_{30}H_{32}N_2O_6$: C, 69.75; H, 6.24; N, 5.42. Found C, 69.88; H, 6.51; N, 5.47; *m/z*: 516.4.

Acknowledgements

We thank for financial support by the open project programme of Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, China (No. 09HJYH04); Hunan Science and Technology Department Project (No. 2009FJ3166) and Hunan Province Undergraduates Innovating Experimentation Project (2009).

References

(1) (a) McDonagh, C.; Burke, C.S.; MacCraith, B.D. *Chem. Rev.* **2008**, *108*, 400–422. (b) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3–40.
(2) Jiang, P.J.; Guo, Z.J. *Coord. Chem. Rev.* **2004**, *248*, 205–229.
(3) Wang, H.H.; Xue, L.; Qian, Y.Y.; Jiang, H. *Org. Lett.* **2010**, *12*, 292–295.
(4) Martin, M.M.; Plaza, P.; Dai, N.H.; Meyer, Y.H.; Bourson, J.; Valeur, B. *Chem. Phys. Lett.* **1993**, *202*, 425–430.
(5) Martin, M.M.; Plaza, P.; Meyer, Y.H.; Begin, L.; Bourson, J.; Valeur, B. *J. Fluoresc.* **1994**, *4*, 271–275.
(6) Delmond, S.; Létard, J.F.; Lapouyade, R.; Mathevet, R.; Jonusauskas, G.; Rullière, C. *New J. Chem.* **1996**, *20*, 861–865.
(7) Fery-Forgues, R.; Le Bris, M.T.; Guette, J.P.; Valeur, B. *J. Chem. Soc. Chem. Commun.* **1988**, *5*, 384–385.
(8) Cazaux, L.; Faher, M.; Lopez, A.; Picard, C.; Tisnes, P. *J. Photochem. Photobiol. A: Chem.* **1994**, *77*, 217–225.
(9) Ahmad, A.R.; Mehta, L.K.; Parrick, J. *Tetrahedron* **1995**, *51*, 12899–12910.
(10) Thomas, K.J.; Manojkumar, T.K.; Das, S.; George, M.V. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1994**, *106*, 1375–1378.
(11) Waldeck, D.H. *Chem. Rev.* **1991**, *91*, 415–436.
(12) Cao, J.; Feng, J.X.; Wu, Y.X.; Tuo, Y.Y. *Chin. Chem. Lett.* **2010**, *21*, 935–938.
(13) William, J.A. *J. Org. Chem.* **1959**, *24*, 282–284.
(14) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill Book Company: New York, 1977, 345–346.
(15) Drake, J.M.; Lesiecki, M.L.; Camaioni, D.M. *Chem. Phys. Lett.* **1985**, *113*, 530–534.
(16) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley: New York, 2001, 292–293.
(17) Bourson, J.; Valeur, B. *J. Phys. Chem.* **1989**, *93*, 3871–3876.
(18) Connors, K.A. *Binding Constants*; Wiley: New York, 1987, 171–373.