Organic &
Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 1287

Received 29th December 2020,
Accepted 19th January 2021

DOI: 10.1039/d0ob02587a

rsc.li/obc

Supramolecular brush polymers prepared from 1,3,4-oxadiazole and cyanobutoxy functionalised pillar[5]arene for detecting Cu^{2+}†

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A supramolecular brush polymer Poly(P5-OXD) was constructed through the self-assembly of an A1/A2 disubstituted pillar[5]arene P5-OXD with a 1,3,4-oxadiazole unit and a cyanobutoxy group, exhibiting external stimuli responsiveness towards Cu^{2+} ions with an ON/OFF fluorescence signal output.

In comparison with the general covalent bond-based polymers, supramolecular polymers have many interesting capabilities such as self-reparability, degradability and self-adaptation due to the nature of the dynamic and reversible noncovalent bonds involved.[1] In addition, the noncovalent bonds provide a possibility of efficiently integrating multiple functions and properties together *via* particular design and control at the molecular level.[2] Thus, supramolecular polymers are ideal candidates for preparing functional materials and smart devices, attracting much attention in the fields of sensors,[3] gels,[4] chemistry topology[5] and advanced materials.[6]

Pillararenes, a special macrocyclic host discovered in 2008,[7] have been widely used in molecular recognition,[8] separations,[9] light-harvesting systems,[10] transmembrane channels,[11] and drug delivery.[12] Recently, pillararenes have also been used as building blocks to construct various supramolecular polymers through the host–guest interactions between the columnar electron-rich cavity and various electron-accepting cationic or neutral guest molecules.[13] To date, great progress has been achieved in pillararene-based supramolecular polymers (PSPs). However, there are still some limitations in this field. For example, such types of supramolecular polymers were mainly constructed by the self-assembly of mono-functionalised pillararene *via* a "head-to-tail" molecular recognition type,[14] leading to the formation of only one-dimensional (1D) linear supramolecular architectures, as well as limited applications in chemical topology. Besides the linear PSPs, other architectural types such as hyperbranched and cross-linked PSPs with three-dimensional (3D) topological structures have also been reported recently. This type of PSP often exhibited reversible and tunable properties, and has presented potential applications in the fields of bio-medicine and materials chemistry. However, the 3D PSPs were always constructed with pillararene-based host monomers and additional guest monomers, which made the supramolecular system too complicated and difficult to further manufacture various polymeric devices.[15]

In recent years, 1,3,4-oxadiazole (OXD) derivatives have found many practical applications in the areas of organic light-emitting diodes (OLEDs)[16] and liquid crystals[17] due to the high photoluminescence quantum yield and excellent chemical stability. Furthermore, the OXD unit has potential metal coordination sites (N and O) towards metal cations, and thus could be used as a signaling component in fluorescent chemosensors for various cations such as Cu^{2+},[18] Zn^{2+},[19] Cd^{2+} [20] and Ag^{+}.[21] However, the application of 1,3,4-oxadiazole derivatives in the fabrication of advanced topological supramolecular self-assemblies is limited up to now.

Here, to build fresh supramolecular brush polymers and develop fluorescent chemosensors with high selectivity towards metal ions, a new pillar[5]arene derivative **P5-OXD** (Scheme 1) was designed and synthesised. The novel structure **P5-OXD** contains a cyanobutoxy group as a guest moiety, which could recognise the electron-rich columnar pillararene cavity, as well as a 1,3,4-oxadizole subunit as a fluorescent and signaling component threading out of supramolecular polymers such as brushes, and the brush structure could enhance the capacity of coordinating targeted metal ions. The formation of **Poly(P5-OXD)**-based supramolecular brush polymers was further fully characterised by ^1H NMR, ^{13}C NMR and scanning electronic microscopy (SEM). The fluorescence properties of the supramolecular brush polymer were investigated, and a

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† Electronic supplementary information (ESI) available: Full experimental details and characterization data including copies of NMR and HRMS spectroscopy of the products. See DOI: 10.1039/d0ob02587a

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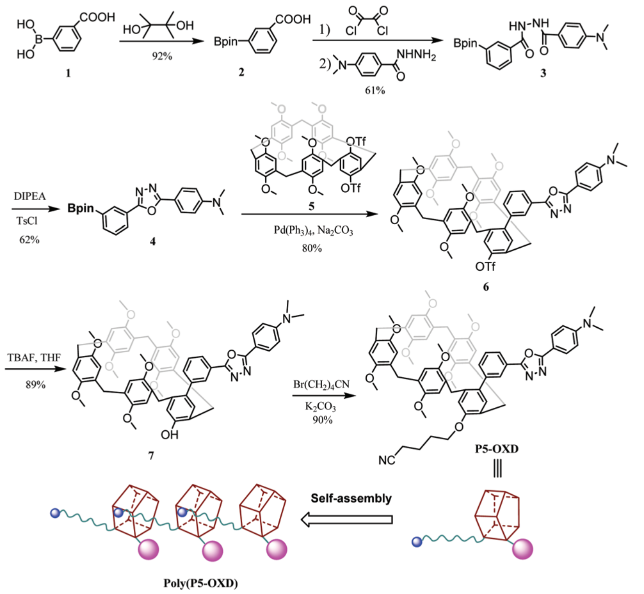
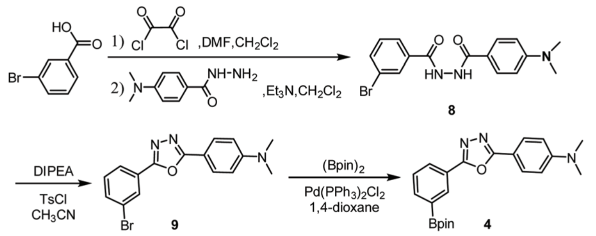


Scheme 1 Synthetic route to **P5-OXD** and the supramolecular polymer **Poly(P5-OXD)**.



Scheme 2 Alternative synthetic route for the intermediate compound **4**.

typical aggregation-induced quenching (AIQ) phenomenon was observed accompanied by a red-shift of the emission wavelength from 411 nm to 426 nm. Upon the addition of Cu^{2+} ions to the chloroform solution of **Poly(P5-OXD)**, a significant decrease of the fluorescence intensity was found.

As seen in Scheme 1, *N*,*N*-dimethyl-4-(5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazol-2-yl) aniline **4** is a key intermediate compound to the synthesis of the target molecule. Initially, compound **4** was designed and synthesised through three steps of reactions as shown in Scheme 2. In this synthetic route, 4-(5-(3-bromophenyl)-1,3,4-oxadiazol-2-yl)-*N*,*N*-dimethylaniline **9** was obtained smoothly in good yield from the economically available 3-bromobenzoic acid as the starting material. However, in the Suzuki-coupling reaction between **9** and 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane), (Bpin)$_2$, only about 60% of **9** could transform into the intermediate **4**. Furthermore, it is difficult to separate the reaction mixture by means of recrystallisation or column chromatography due to the similar solubility and polarity of the reagents and product. In contrast, the intermediate **4** was successfully obtained in a total yield of 34.8% *via* three steps of reactions as shown in Scheme 2. Then, the product **P5-OXD** was prepared in high yield through Suzuki-coupling reaction between the intermediates **4** and **5**, deprotection of the triflate ester of **6** and introduction of a cyanobutoxy group to **7** by substitution reaction.

The formation of the supramolecular polymer was firstly investigated by means of proton nuclear magnetic resonance (NMR). The ^{1}H NMR spectroscopy results of **P5-OXD** and 5-bromopentanenitrile are shown in Fig. 1. All proton signals of **P5-OXD** were broad, and the signals derived from the cyanobutoxy group (H$_b$, H$_c$ and H$_d$) shifted upfield remarkably due to the shielding effect of the electron-rich cavities of pillar[5]arene suggesting that the neutral cyanobutoxy group was threaded in the electron-rich cyclic cavity of **P5-OXD** *via* host–guest interactions to form a supramolecular polymer with a bigger-sized and electron-rich 1,3,4-oxadizole subunit threading out of supramolecular polymers like brushes.[22] Moreover, ^{1}H–^{1}H NOESY experiments were also performed (Fig. 2), and correlation signals were observed between protons on cyanobutoxy and aromatic protons as well as the bridging methylene protons on the pillar[5]arene skeleton, suggesting that the cyanobutoxy group was threaded in the cyclic cavity of **P5-OXD** to form a linear supramolecular polymer.

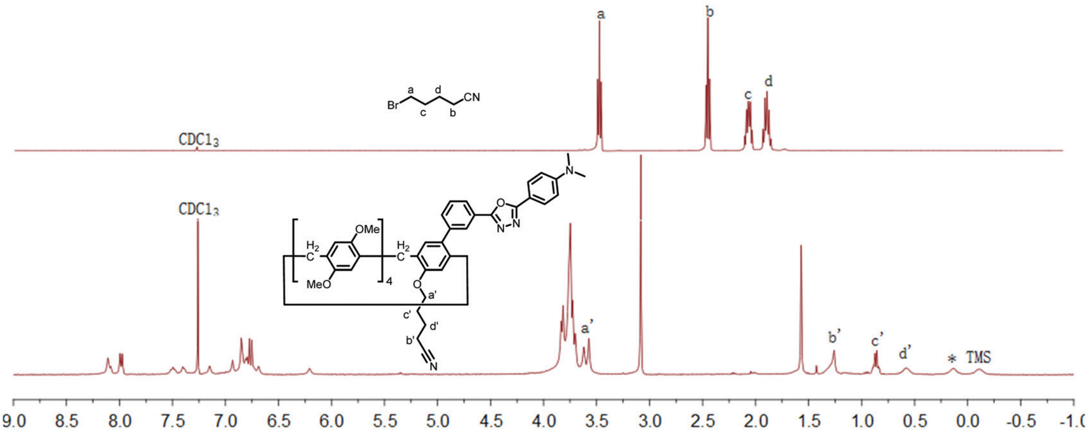


Fig. 1 ^{1}H NMR spectra (400 MHz, CDCl$_3$, 298 K) of (a) **P5-OXD** (20 mM) and (b) 5-bromopentanenitrile (*solvent peaks).

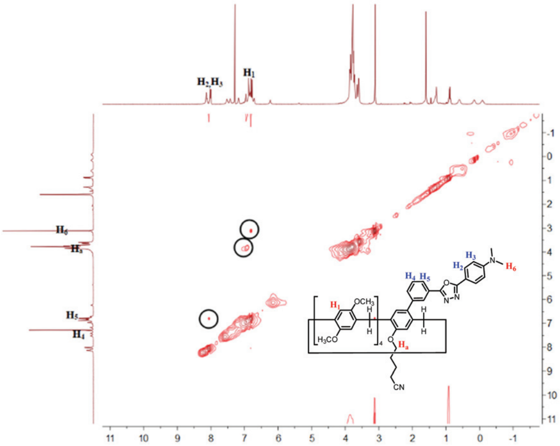


Fig. 2 $^1H-^1H$ NOESY analysis of **P5-OXD** (20 nM) (400 MHz, $CDCl_3$, 298 K).

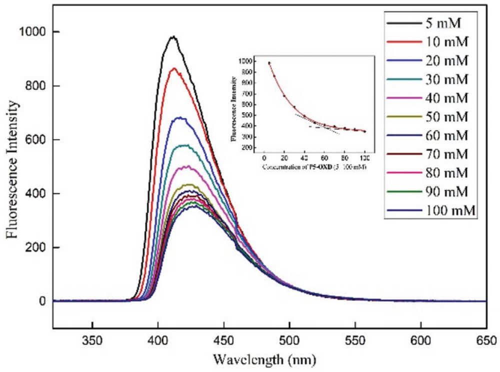


Fig. 3 Changes in the fluorescence emission spectra of **P5-OXD** with different concentrations in chloroform (λ_{ex} = 310 nm), and the fluorescence intensity *versus* **P5-OXD** concentration (inset).

The changes in the fluorescence emission spectra of **P5-OXD** under different concentrations in chloroform were investigated, also indicating the formation of the supramolecular brush polymer. As shown in Fig. 3, under irradiation with UV-light (310 nm), the solution of **P5-OXD** in chloroform (5 mM) displayed a strong emission (λ_{max} = 411 nm). With the increase of the concentration of **P5-OXD**, the intensity of the emission decreased dramatically with a slight red-shift from 411 nm to 426 nm, indicating the gradual formation of supramolecular brush polymers due to the aggregation-caused quenching. Notably, as the concentration was increased up to 60 mM, the fluorescence intensity gradually tended to remain unchanged, indicating that the critical aggregation concentration of **P5-OXD** is achieved.

Furthermore, the morphology of the supramolecular brush polymer was investigated by SEM. By rapid drying of an equimolar mixture of **P5-OXD** in chloroform (60 mM), bundles of a rod-like crystalline precipitate was observed, providing direct evidence for the formation of supramolecular brush architectures (Fig. 4).

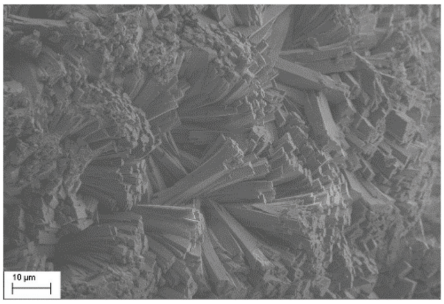


Fig. 4 SEM image of the supramolecular assembly prepared from **P5-OXD** in chloroform.

Because the supramolecular brush polymer **Poly(P5-OXD)** can emit strong fluorescence by controlling the concentration, and the "brush-like" 1,3,4-oxadiazole subunits attached to the supramolecular polymers may enhance the metal coordination with Cu^{2+} ions, self-assemblies of **Poly(P5-OXD) were** further used as a fluorescent chemosensor for Cu^{2+}. The fluorescence change of **Poly(P5-OXD)** was investigated briefly by the addition of increasing amounts of Cu^{2+} to its solution in chloroform. The fluorescence intensity (Fig. 5) at the position of the emission maxima decreased gradually with the increase of the loading amount of Cu^{2+}. About 1 equiv. of Cu^{2+} makes the quenched fluorescence reach a minimum plateau. It was supposed that upon the addition of Cu^{2+} ions, the supramolecular brush polymer might coordinate with metal cations *via* the 1,3,4-oxadiazole-based brushes, and further form a cross-linked supramolecular network accompanied by the quenching of the fluorescence.[23,18a,b] Thus, **Poly(P5-OXD)** shows the possibility of application in a potential fluorescent chemosensor for Cu^{2+} ions. The specific recognition of Cu^{2+} might be rationalised by Irving–Williams order stability in terms of complex formation.[24] Cu^{2+} is a well-known paramagnetic ion with an unfilled *d* shell and could strongly quench the fluorescence of a fluorophore through electron or energy transfer between the metal cation and the fluorophore.[18a]

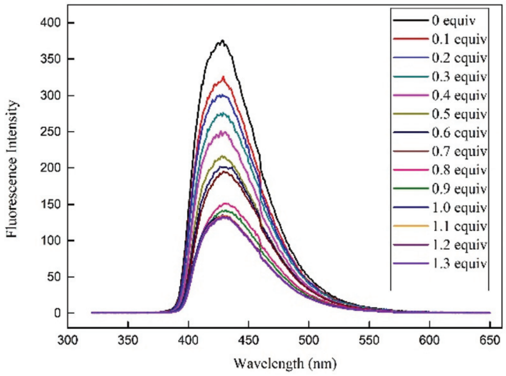


Fig. 5 Fluorescence spectra (λ_{ex} = 310 nm) of **Poly(P5-OXD)** in chloroform (the concentration of **P5-OXD** is 60 mM) with various equivalents of Cu^{2+} (0–1.3 equiv.).

In summary, an A1/A2 disubstituted pillar[5]arene (**P5-OXD**) was first synthesised by modifying the pillar[5]arene skeleton with a 1,3,4-oxadiazole subunit and a cyanobutoxy moiety, and **P5-OXD** was used to fabricate the supramolecular brush polymers by host–guest interactions between electron-rich pillararene cavities and proper-sized neutral cyanobutoxy moieties. Particularly, the bigger-sized electron-deficient 1,3,4-oxadiazole subunit stays outside the pillararene cavities after the formation of host–guest inclusions, functioning as "brushes" to enhance the capacity of self-assembled supramolecular materials in coordinating with metal ions such as Cu^{2+}. As confirmed by NMR, SEM and spectral studies, after the addition of Cu^{2+} ions, the supramolecular brush polymer exhibits different structural information in accordance with fluorescence quenching, indicating the possibility of changing into cross-linked supramolecular networks. Thus, this supramolecular brush polymer has potential applications in fluorescent chemosensors for metal cations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the Natural Science Foundation of Tianjin (No. 18JCYBJC20700), which is gratefully acknowledged. HZ is thankful for the financial support for academic research studies from "Young Talent Support Plan" (No. 0001-7121191207 and No. 0107-712110510706) of Xi'an Jiaotong University and "Thousand Talents Program" of Shaanxi Province (No. 0578-7122200046).

Notes and references

1 (*a*) H. Li, Y. Yang, F. F. Xu, T. X. Liang, H. R. Wen and W. Tian, *Chem. Commun.*, 2019, **55**, 271–285; (*b*) Z. F. He, Y. F. Huo, C. Wang, D. Pan, B. B. Dong, M. L. Wang, L. Guo, Z. L. Hu and Z. H. Guo, *Chem. Commun.*, 2020, **56**, 9288–9291; (*c*) J. Park, S. Murayama, M. Osaki, H. Yamaguchi, A. Harada, G. Matsuba and Y. Takashima, *Adv. Mater.*, 2020, **32**, 2002008; (*d*) J. Hatai, C. Hirschhaeuser, J. Niemeyer and C. Schmuck, *ACS Appl. Mater. Interfaces*, 2020, **12**, 2107–2115; (*e*) C. H. Xu, J. D. Nie, W. C. Wu, Z. J. Zheng and Y. K. Chen, *ACS Sustainable Chem. Eng.*, 2019, **7**, 15778–15789; (*f*) T. Kakuta, T. A. Yamagishi and T. Ogoshi, *Acc. Chem. Res.*, 2018, **51**, 1656–1666.

2 (*a*) B. Li, T. He, Y. Q. Fan, X. C. Yuan, H. Y. Qiu and S. C. Yin, *Chem. Commun.*, 2019, **55**, 8036–8059; (*b*) Z. C. Gao, C. P. Wei, Y. F. Han, M. Yuan, X. Z. Yan and F. Wang, *Chin. J. Polym. Sci.*, 2018, **36**, 399–405.

3 (*a*) T. T. Liu, S. D. Wang, Y. R. Li, H. X. Yan and W. Tian, *Chem. – Eur. J.*, 2018, **24**, 4239–4244; (*b*) T. L. Mako, J. M. Racicot and M. Levine, *Chem. Rev.*, 2019, **119**, 322–477.

4 (*a*) J. X. He, Y. M. Zhang, J. P. Hu, Y. J. Li, Q. Zhang, W. J. Qu, H. Yao, T. B. Wei and Q. Lin, *Appl. Organomet. Chem.*, 2020, **34**, e5519; (*b*) X. F. Ji, X. D. Chi, M. Ahmed, L. L. Long and J. L. Sessler, *Acc. Chem. Res.*, 2019, **52**, 1915–1927; (*c*) Y. Z. Liu, Y. Y. Zhang, H. T. Z. Zhu, H. Wang, W. Tian and B. B. Shi, *Mater. Chem. Front.*, 2018, **2**, 1568–1573; (*d*) L. Shao, J. Yang and B. Hua, *Polym. Chem.*, 2018, **9**, 1293–1297.

5 J. W. Yang, R. B. Bai, B. H. Chen and Z. G. Suo, *Adv. Funct. Mater.*, 2020, **30**, 1901693.

6 (*a*) W. W. Feng, M. Jin, K. Yang, Y. X. Pei and Z. C. Pei, *Chem. Commun.*, 2018, **54**, 13626–13640; (*b*) X. Li, Z. Li and Y. W. Yang, *Adv. Mater.*, 2018, **30**, e1800177; (*c*) Y. F. Han, Y. K. Tian, Z. J. Li and F. Wang, *Chem. Soc. Rev.*, 2018, **47**, 5165–5176; (*d*) O. J. G. M. Goor, S. I. S. Hendrikse, P. Y. W. Dankersand and E. W. Meijer, *Chem. Soc. Rev.*, 2017, **46**, 6621–6637; (*e*) E. Krieg, M. M. C. Bastings, P. Beseniusand and B. Rybtchinski, *Chem. Rev.*, 2016, **116**, 2414–2477; (*f*) X. Ma and Y. L. Zhao, *Chem. Rev.*, 2015, **115**, 7794–7839.

7 T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022–5023.

8 (*a*) L. S. Yakimova, D. N. Shurpik, L. H. Gilmanova, A. R. Makhmutova, A. Rakhimbekova and I. I. Stoikov, *Org. Biomol. Chem.*, 2016, **14**, 4233–4238; (*b*) D. Dai, Z. Li, J. Yang, C. Wang, J.-R. Wu, Y. Wang, D. Zhang and Y.-W. Yang, *J. Am. Chem. Soc.*, 2019, **141**, 4756–4763; (*c*) K.-A. Li, Z. Wang, C.-D. Xie, T. Chen, H. Qiang, Y. A. Liu, X.-S. Jia, W.-B. Hu and K. Wen, *Org. Biomol. Chem.*, 2019, **17**, 4975–4978.

9 K. Jie, Y. Zhou, E. Li and F. Huang, *Acc. Chem. Res.*, 2018, **51**, 2064–2072.

10 S. Guo, Y. Song, Y. He, X.-Y. Hu and L. Wang, *Angew. Chem., Int. Ed.*, 2018, **57**, 3163–3167.

11 W. Si, P. Y. Xin, Z. T. Li and J. L. Hou, *Acc. Chem. Res.*, 2015, **48**, 1612–1619.

12 N. Song, X.-Y. Lou, L. Ma, H. Gao and Y.-W. Yang, *Theranostics*, 2019, **9**, 3075–3093.

13 (*a*) H. C. Zhang and J. Han, *Org. Biomol. Chem.*, 2020, **18**, 4894–4905; (*b*) H. Li, Z. Duan, Y. Yang, F. Xu, M. Chen, T. Liang, Y. Bai and R. Li, *Macromolecules*, 2020, **53**, 4255–4263; (*c*) H. Li, W. Chen, F. Xu, X. Fan, T. Liang, X. Qi and W. Tian, *Macromol. Rapid Commun.*, 2018, **39**, 1800053.

14 (*a*) X. Y. Yang, W. Q. Cai, S. Dong, K. Zhang, J. Zhang, F. H. Huang, F. Huang and Y. Cao, *ACS Macro Lett.*, 2017, **6**, 647–651; (*b*) S. L. Wang, Y. L. Wang, Z. X. Chen, Y. J. Lin, L. H. Weng, K. Han, J. Li, X. S. Jia and C. J. Li, *Chem. Commun.*, 2015, **51**, 3434–3437.

15 (*a*) J. F. Chen, Q. Lin, Y. M. Zhang, H. Yao and T. B. Wei, *Chem. Commun.*, 2017, **53**, 13296–13311; (*b*) L. L. Yang, X. X. Tan, Z. Q. Wang and X. Zhang, *Chem. Rev.*, 2015, **115**, 7196–7239.

16 A. Paun, N. D. Hadade, C. C. Paraschivescu and M. Matache, *J. Mater. Chem. C*, 2016, **4**, 8596–8610.

17 (*a*) J. Han, *J. Mater. Chem. C*, 2013, **1**, 7779–7797; (*b*) J. Han, Z. Q. Xi, F. L. Wang, L. H. Bu and Y. M. Wang, *Dyes Pigm.*, 2018, **154**, 234–241.

18 (*a*) J. Han, F. L. Wang, Y. X. Liu, F. Y. Zhang, J. B. Meng and Z. J. He, *ChemPlusChem*, 2012, **77**, 196–200; (*b*) D. H. Xie, X. J. Wang, C. Sun and J. Han, *Tetrahedron Lett.*, 2016, **57**, 5834–5836; (*c*) S. Liu, Y. Wang and J. Han, *J. Photochem. Photobiol., C*, 2017, **32**, 78–103.

19 L. Lin, D. Wang, S. H. Chen, D. J. Wang and G. D. Yin, *Spectrochim. Acta, Part A*, 2017, **174**, 272–278.

20 X. L. Tang, X. H. Peng, W. Dou, J. Mao, J. R. Zheng, W. W. Qin, W. S. Liu, J. Chang and X. J. Yao, *Org. Lett.*, 2008, **10**, 3653–3656.

21 C. L. Zheng, A. L. Yuan, Z. Y. Zhang, H. Shen, S. Y. Bai and H. B. Wang, *J. Fluoresc.*, 2013, **23**, 785–791.

22 (*a*) S. L. Wang, Y. L. Wang, Z. X. Chen, Y. J. Lin, L. H. Weng, K. Han, J. Li, X. Jia and C. J. Li, *Chem. Commun.*, 2015, **51**, 3434–3437; (*b*) L. B. Meng, D. Li, S. Xiong, X. Y. Hu, L. Wang and G. Li, *Chem. Commun.*, 2015, **51**, 4643–4646.

23 (*a*) Q. Lin, B. Sun, Q. P. Yang, Y. P. Fu, X. Zhu, T. B. Wei and Y. M. Zhang, *Chem. – Eur. J.*, 2014, **20**, 11457–11462; (*b*) Q. Lin, Y. Q. Fan, P. P. Mao, L. Liu, J. Liu, Y. M. Zhang, H. Yao and T. B. Wei, *Chem. – Eur. J.*, 2018, **24**, 777–783; (*c*) L. Wang, Q. J. Bing, J. X. Li and G. Wang, *J. Photochem. Photobiol., A*, 2018, **360**, 86–94.

24 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192–3210.