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1 Introduction

Fluorescent sensors that are capable of sensing various biologically and/or chemically important anionic species are emerging as a research area of great importance.1 One of the more attractive subjects in this field involves the construction of chemosensors. In this context, two-photon fluorescent chemosensors can provide exclusive confinement of the excitation to the focal volume with high 3-dimensional resolution and reduced photobleaching and phototoxicity by virtue of the lowenergy NIR excitation (700-1000 nm), and the development of novel two-photon-excitable sensors has been an area of intensive research.² Until now, a variety of organic two-photon absorption (2PA) molecules with large 2PA cross-sections (δ) and strong two-photon excited fluorescence (2PEF) have been extensively developed, however, most of the 2PA dyes reported in the literature to date employ carbon-carbon double bonds as conjugation bridges, and the 2PA molecules with stable chemical structure such as fully aromatic compounds exhibiting

N-Monoalkylated 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrroles as effective one- and two-photon fluorescence chemosensors for fluoride anions†

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We have synthesized three *N*-monoalkylated DPP (mDPP) derivatives, 3,6-bis(4-chloro-/methyl-/bromophenyl)-2-octyl-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-diones (mDPP-Cl/mDPP-Me/mDPP-Br), by facile onestep monoalkylation of commercially available or easy-prepared corresponding DPP derivatives. All the three compounds have high fluorescence quantum yields (Φ) and exhibit usable two-photon absorption cross-sections ($\delta = 58-87$ GM). They are not only effective one-photon but also more effective twophoton fluorescence chemosensors selectively for fluoride anions. Moreover, the substituents at the benzene ring, even if simple methyl, chloride and bromide, could affect the intramolecular charge transfer from the lactam N to the DPP core, and the sensing performance of mDPP to fluoride ions is in the order, mDPP-Br \ge mDPP-Cl > mDPP-Me. Proton NMR titrations indicate that the intermolecular proton transfer between the hydrogen atom on the lactam N and the fluoride anion is the sensing origin. The stable chemical structure, small molecular size and usable $\Phi\delta$ in terms of femto-second laser pulses make mDPP moieties suitable for the construction of new and effective fully aromatic twophoton materials applicable in two-photon science and technology.

> usable δ and 2PEF are rather rare.² Moreover, the 2PA molecules that can sense ions and biological species are limited,^{2,3} and the mostly reported two-photon fluorescent sensors are based on the fluorescence quenching or enhancement caused by the bound species. It is known that the fluorescence intensity could be affected by many other poorly quantified or variable factors, such as photobleaching, sensor concentration, the environment around the sensor molecules (polarity, temperature, and so forth) and the stability of the sensory system under illumination. Therefore, to increase the selectivity and sensitivity, colorimetric, ratiometric and fluorometric sensors involving the changes of the absorption, the emission intensity and fluorescence color at two interval wavelengths are desirable.

> Fluoride anion has unique chemical and physiological properties, and it is also associated with nerve gases, analysis of drinking water, and the refinement of uranium.⁴ Therefore, it is necessary for environmental or biological systems to develop the effective two-photon fluorescent sensors selectively for fluoride. However, to the best of our knowledge, there are only a few reports on two-photon fluorescent sensors for fluoride⁵ although a variety of one-photon fluorescent sensors for fluoride⁵ although a variety of one-photon fluorescent sensors for fluoride in developing 1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) derivatives as effective two-photon fluorescent sensors for fluoride anions. This is mainly because (i) DPP derivatives represent a class of brilliant red and strongly fluorescent high

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[†] Electronic supplementary information (ESI) available: The details for synthesis and characterization, and the normalized absorption and emission spectra. See DOI: 10.1039/c3ta00160a



Scheme 1 The synthesis and structure of *N*-monoalkylated DPP derivatives (**mDPP-X**) and the possible mechanism for sensing fluoride anions.

performance pigments and have exceptional light, weather and heat stability;7 (ii) DPP derivatives have been used to construct highly luminescent, electroactive and photoactive materials in optical and opto-electronic fields;8 (iii) the intermolecular proton transfer of the hydrogen atom at the lactam N positions of DPP, like other pyrrole-based derivatives,9 could take place only upon adding fluoride anions, which has been used as onephoton fluorescent sensors for fluoride anions.9e More importantly, we recently have confirmed that DPP itself and its organic and polymeric derivatives exhibit large δ and high fluorescence quantum yield (Φ) .¹⁰ With the findings above, it is expected that N-monoalkylated DPP (mDPP) derivatives should be promising candidates for the two-photon fluorescent sensors of fluoride anions. We now report that N-monoalkylated commercially available simple DPP derivatives (shown in Scheme 1) could operate as effective ratiometric and fluorometric two-photon chemosensors selectively for fluoride anions.

2 Results and discussion

2.1 Synthesis and characterization of mDPP-X

mDPP-Cl, mDPP-Br and **mDPP-Me** are synthesized facilely by one-step monoalkylation of the lactam units of commercially available 3,6-bis(4-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*, 5*H*)-dione, 3,6-di-*p*-tolylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione, and easy-prepared 3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (Scheme 1). The monoalkyl and dialkyl DPP derivatives can be easily separated by using flash column chromatography because of their different polarities. The target products were unambiguously characterized by NMR spectra (¹H and ¹³C) and elemental analysis.

2.2 One-photon photophysical properties of mDPP-X

The one-photon absorption and emission spectra of three **mDPP-X** compounds in THF are shown in Fig. 1, and the corresponding spectral data are summarized in Table 1. The absorption spectra of three **mDPP-X** possess the same shape, but the absorption bands of **mDPP-Cl** and **mDPP-Br** are red-shifted by 6 and 8 nm respectively compared to that of **mDPP-Me** (Fig. 1, left). Similarly, their emission spectra are all of the same shape, but the red-shift emission bands of 8 and 11 nm for



Fig. 1 Absorption (left) and emission (right) spectra of mDPP-Me, mDPP-Cl and mDPP-Br in THF (1.0×10^{-5} M).

Table 1 Photophysical data for mDPP-Cl, mDPP-Br and mDPP-Me in THF

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							
mDPP-Me 495 526 1190 0.61 87.4 53.5 mDPP-Me + F^- 577 525,605 802 0.39 22.1 8.5 MDPP-Cl 501 534 1268 0.56 58.5 32.5 mDPP-Cl + F^- 595 535,623 730 0.42 30.7 12.5 mDPP-Br 503 537 1224 0.52 74.2 38.5 mDPP-Br + F^- 597 536,626 776 0.32 56.5 18.5	Solution	$\lambda_{ m abs}{}^a$ (nm)	$\lambda_{em}^{\ b}$ (nm)	$\Delta \tilde{\nu}^c$ (cm ⁻¹)	Φ^d	δ^e (GM)	$\Phi\delta^f$ (GM)
mDPP-Me + F^- 577 525, 605 802 0.39 22.1 8. MDPP-Cl 501 534 1268 0.56 58.5 32. mDPP-Cl + F^- 595 535, 623 730 0.42 30.7 12. mDPP-Br 503 537 1224 0.52 74.2 38. mDPP-Br + F^- 597 536, 626 776 0.32 56.5 18.	mDDD-Me	495	526	1100	0.61	87 /	53.3
mDPP-Me + F ⁻ 577 525,605 802 0.39 22.1 8. MDPP-Cl 501 534 1268 0.56 58.5 32. mDPP-Cl + F ⁻ 595 535,623 730 0.42 30.7 12. mDPP-Br 503 537 1224 0.52 74.2 38. mDPP-Br + F ⁻ 597 536,626 776 0.32 56.5 18.	IIIDI I -MIC	495	520	1190	0.01	07.4	55.5
MDPP-Cl 501 534 1268 0.56 58.5 32. mDPP-Cl + F ⁻ 595 535, 623 730 0.42 30.7 12. mDPP-Br 503 537 1224 0.52 74.2 38. mDPP-Br + F ⁻ 597 536, 626 776 0.32 56.5 18.	$mDPP-Me + F^{-}$	577	525,605	802	0.39	22.1	8.7
mDPP-Cl + F ⁻ 595 535, 623 730 0.42 30.7 12. mDPP-Br 503 537 1224 0.52 74.2 38. mDPP-Br + F ⁻ 597 536, 626 776 0.32 56.5 18.	MDPP-Cl	501	534	1268	0.56	58.5	32.8
mDPP-Br 503 537 1224 0.52 74.2 38. mDPP-Br + F ⁻ 597 536, 626 776 0.32 56.5 18.	$mDPP-Cl + F^{-}$	595	535, 623	730	0.42	30.7	12.9
mDPP-Br + F^- 597 536, 626 776 0.32 56.5 18.	mDPP-Br	503	537	1224	0.52	74.2	38.6
	$mDPP-Br + F^{-}$	597	536, 626	776	0.32	56.5	18.1

^{*a*} The peak wavelength of the lowest energy one-photon absorption band. ^{*b*} Peak wavelength of the one-photon fluorescence spectra. ^{*c*} Stokes shift. ^{*d*} Fluorescence quantum yield. ^{*e*} 2PA cross-sections at 720 nm. ^{*f*} Two-photon action cross-sections at 720 nm.

mDPP-Cl and **mDPP-Br** respectively over that of **mDPP-Me** are observed (Fig. 1, right). The solution fluorescence quantum yields (Φ) of **mDPP-X** are also relative to the substituents at the benzene ring, and Φ values of **mDPP-Br**, **mDPP-Cl** and **mDPP-Me** in THF measured by the dilute solution method using rhodamine B as the reference are 0.56, 0.52 and 0.61, respectively. Overall, they are all strongly fluorescent molecules, and the substituents at the benzene ring of DPP, even if simple methyl, chloride and bromide, could affect the intramolecular charge transfer (ICT) effect of the DPP core and modify moderately the optical properties of DPP derivatives.

2.3 One-photon responses of mDPP-X to fluoride ions

One-photon absorption and emission spectra of **mDPP-X** in THF with the progressive addition of n-Bu₄NF (TBAF) are shown in Fig. 2 and 3, where the TBAF was used as a fluoride source. The corresponding spectroscopic data are summarized in Table 1. Overall, the absorption bands centered at *ca.* 480 nm were gradually decreased, at the same time, the completely new absorption bands at 575 nm for **mDPP-Me** and *ca.* 595 nm for **mDPP-Cl** and **mDPP-Br** appeared and were developed with the addition of fluoride anions (Fig. 2). This indicates the formation

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of new optical species with a stronger push–pull electron effect and the emergence of ratiometric and colorimetric sensors for fluoride anions. The fluorescence emission spectra show that the original emission bands peaked at *ca*. 530 nm with a gradual decrease in the emission shoulder at 570 nm, at the same time, new emission peaks at 605 nm for **mDPP-Me** and *ca*. 625 nm for **mDPP-Cl** and **mDPP-Br** are gradually developed with the addition of fluoride anions (Fig. 3). This implies that **mDPP-X** is also fluorometric sensors for fluoride anions. The decrease of original absorption and emission bands and the increase of new absorption and emission bands with the addition of fluoride anions can be observed more clearly by normalizing the spectra (Fig. S1 and S2[†]).

Fluoride, an anion with high charge density and small size, is a strong proton transfer acceptor and can interact with amide derivatives containing proton transfer donor groups.⁹ In order to understand the spectral changes upon addition of fluoride anions, the partial ¹H NMR spectra of **mDPP-X** in CDCl₃ in the presence and absence of TBAF are recorded (Fig. 4). It is found that the proton signals of lactam NH at the high δ zone disappear when an excess amount of F⁻ was added. This confirms the assumption of intermolecular proton transfer (IPT) between a hydrogen atom at the lactam N positions of the DPP moiety and the fluoride anion (Scheme 1). Undoubtedly, the IPT process can directly influence the intramolecular charge transfer (ICT) from the lactam N anion (electron donor) to the DPP core (electron acceptor). In the presence of fluoride, this ICT effect is

enhanced by the deprotonation of the lactam moiety, which should be responsible for the appearance of the new longwavelength absorption and emission bands. The fluorescence quantum yields (Φ) of three compounds in the presence of TBAF ([**mDPP-CI**]/[F⁻] = [**mDPP-Br**]/[F⁻] = 6/1, [**mDPP-Me**]/[F⁻] = 12/1) are measured in THF. The results show that the Φ values for **mDPP-Cl**, **mDPP-Br** and **mDPP-Me** are 0.42, 0.32 and 0.39, respectively, indicating that they are still highly fluorescent upon addition of fluoride anions.

Since the spectral changes of mDPP derivatives result from the IPT process between the hydrogen atom at the lactam N position of the DPP moiety and a fluoride anion, the substituent at the benzene ring of DPP should affect the ICT effect and then influence the sensing properties of mDPP derivatives for fluoride anions. It is found that the decrease of the short-wavelength absorption and emission bands relative to electronically neutral species (Ar-DPP-NH-Ar) for mDPP-Cl and mDPP-Br and the increase of the long-wavelength ones relative to negatively charged species (Ar-DPP-N⁻-Ar) are faster than those of mDPP-Me upon addition of TBAF (Fig. 2 and 3). Moreover, although the absorption and emission spectra of three compounds are similar (Fig. 1), the absorption and emission bands of negatively charged mDPP-Cl and mDPP-Br are significantly red shifted compared to those of negatively charged mDPP-Me (Fig. S2, S3⁺ and Table 1). Fig. 4 also shows that the amide NH proton signals (single peak at high δ zone) of **mDPP-Cl** and **mDPP-Br** disappear at a relatively low concentration of TBAF, and those of



Fig. 4 The partial ¹H NMR spectra of mDPP-X in $CDCI_3$ in the presence of different equivalents of n-Bu₄NF.

mDPP-Me disappear at a relatively high concentration of TBAF. Fig. 5a shows the photographs of fluorescence color changes of three compounds in THF with different equivalents of TBAF. Notable fluorescence color changes are observed for **mDPP-Cl** and **mDPP-Br** compared to **mDPP-Me** under the same equivalents of fluoride anions. The results above indicate that **mDPP-Cl** and **mDPP-Br** are better colorimetric, ratiometric and fluorometric sensors for fluoride ions. It seems that the electronwithdrawing substituents incorporated at the benzene ring could improve the sensing properties due to the enhanced push-pull electron effect.

To examine the selectivity of the three sensors towards fluoride anions, we have investigated the fluorescence responses to other available anions such as Cl^- , Br^- , I^- , ClO_4^- , $H_2PO_4^-$, CH_3COO^- , SCN^- , NO_3^- and SO_4^{-2-} (as tetrabuty-lammonium salts). There are no noticeable changes in the fluorescence color upon addition of other anions (Fig. 5b),



Fig. 5 Fluorescence photographs of **mDPP-X** in THF (1.0×10^{-5} M) with different equivalents of fluoride anions (a) and **mDPP-Br** in THF with other anions of 6 equiv. (b) under illumination of a 365 nm UV lamp.

indicating that the mDPP-based compounds are highly selective sensors for fluoride. In addition, the fluoride anion can still be detected when the other anions exist in the same solution, and the addition of only F^- to mDPP solution leads to a remarkable change in the fluorescence color (the first cell in Fig. 5b). That is, only the hard electronically negative F^- can break the N–H bond of the lactam unit to form a red-emitting negatively charged Ar–DPP–N⁻–Ar (Scheme 1).

2.4 Two-photon absorption and fluorescence properties of mDPP-X

Two-photon excited fluorescence (2PEF) spectra measured using femto-second laser pulses (120 fs) as described in the Experimental section are shown in Fig. S3.[†] The 2PEF spectrum of each compound is similar to its one-photon excited fluorescence spectra (Fig. 1), indicating that the one- and two-photon fluorescence occurs from the same excited states, regardless of the mode of excitation. Since there is no one-photon absorption beyond 700 nm for the three compounds (Fig. 2), the fluorescence emission excited by low-energy NIR light must be from the nonlinear absorption. To further confirm the nature of this nonlinear absorption, the emission spectra of **mDPP-CI** under the constant excitation wavelength (720 nm) and the tunable input laser powers of 80–200 mW are recorded (Fig. 6a). We



Fig. 6 Two-photon excitation fluorescence (2PEF) spectra of **mDPP-CI** (1.0×10^{-4} M) before (a) and after (b) adding 6.0 equiv. of TBAF in THF excited at 720 nm under different input laser powers. The inset is the dependence of output fluorescence (signal) intensity on the input laser power.



Fig. 7 Two-photon excitation spectra of mDPP-X (1.0×10^{-4} M in THF) without (a) and with (b) fluoride anions under an input laser power of 150 mW.

have observed that the fluorescence intensity is gradually increased with the input laser power. Moreover, a power-law dependence of exponent 1.99 in the plot of logarithmic output fluorescence intensity (up-conversion signal) *versus* logarithmic input laser power is found (the inset in Fig. 6a), indicative of a two-photon excitation (absorption) process.

Fig. 7a shows the two-photon excitation spectra of the three compounds under an input laser power of 150 mW (which falls within the power range of two-photon excitation, Fig. 6b), and the spectroscopic parameters are summarized in Table 1. It is observed that the 2PA bands are mainly located in the range of 710–800 nm, and **mDPP-Br** is optimal 2PA dye due to the constant large δ value. Overall, the relatively broad 2PA bands, small molecular size, full aromatic structure and usable two-photon fluorescence action cross-sections ($\Phi\delta$) in terms of femto-second laser pulses (Table 1) make these compounds applicable in two-photon science and technology.

2.5 Two-photon responses of mDPP-X to fluoride anions

The above results have demonstrated that **m-DPP-X** could not only be used as one-photon sensors for fluoride ions but also exhibit usable $\Phi \delta$. Therefore, it is interesting to investigate their two-photon sensing properties for fluoride ions. Proton NMR titrations have shown that most **mDPP-X** have changed into negatively charged species (Ar–DPP–N[–]–Ar) when the equiv. of fluoride ions is up to 12.0 for **mDPP-Me** and 6.0 for **mDPP-Br** and **mDPP-Cl**, respectively (Fig. 4). The two-photon excitation spectra of **mDPP-X** under the above concentrations of fluoride anions are shown in Fig. 7b, and the corresponding spectroscopic parameters are summarized in Table 1. It is shown that their 2PA bands are also mainly before 800 nm. Moreover, to a given excitation wavelength, the δ values are in the order, **mDPP-Br** > **mDPP-Cl** > **mDPP-Me**. Although the δ values of mDPP-X are decreased to some extent by the addition of TBAF, they still have usable $\Phi\delta$ due to the high Φ (Table 1). Fig. 8 shows the 2PEF spectra of mDPP-X in THF upon addition of different equivalents of TBAF. It is shown that the 2PEF intensities peaked at ca. 530 nm are also gradually decreased and the new emission bands peaked at ca. 600 nm for mDPP-Me and ca. 625 nm for mDPP-Br and mDPP-Cl appear and increase rapidly with the increase of fluoride anions. This can be observed more clearly from the normalized 2PEF spectra (Fig. S4[†]). This indicates that mDPP-X can be also used as the ratiometric and fluorometric two-photon sensors for fluoride anions. It is interesting to make a comparison between the one- and twophoton sensing properties. The new emission bands relative to negatively charged species (Ar-DPP-N⁻-Ar) become obvious only under high concentrations of fluoride ions for one-photon excitation (Fig. 3); in contrast, notable new emission bands can be observed under low concentrations of fluoride ions for twophoton excitation (Fig. 8). This indicates a higher detection sensitivity of mDPP-X to fluoride ions upon two-photon excitation, which might be due to that the different excitation modes (one- and two-photon) involve different types of excited states. However, the real origin for this intriguing phenomenon is not clear at present.

Careful inspection of the 2PEF spectra of three **mDPP-X** derivatives with TBAF reveals that the emission bands peaked at 535 nm become very weak and the new emission bands relative to Ar–DPP–N[–]–Ar have been close to an independent and perfect profile when the amount of TBAF reaches 2.5 and 1.5 equiv. for **mDPP-Cl** and **mDPP-Br**, respectively (Fig. 8). The obviously higher fluorometric emissions of **mDPP-Br** and **mDPP-Cl** over **mDPP-Me** under the same concentration of fluoride ions indicate that **mDPP-Cl** and **mDPP-Br** are better two-photon fluorescence sensors for fluoride anions. This finding also implies that the subtle manipulation of the substituent at the benzene ring and the conjugation extension of mDPP could endow mDPP derivatives with



Fig. 8 Two-photon excitation fluorescence (2PEF) spectra of **mDPP-X** in THF (1.0×10^{-4} M) with different equivalents of fluoride ions excited at 720 nm under an input laser power of 150 mW.

improved two-photon absorption and sensing properties. Finally, to confirm the nature of the nonlinear absorption of negatively charged species (Ar–DPP–N[–]–Ar), the 2PEF spectra of **mDPP-Cl** with 6 equiv. of TBAF are recorded under a constant excitation wavelength (720 nm) with different input laser powers (80–200 mW) (Fig. 6b). The gradually increased output fluorescence signal intensity with the input laser power affords a power-law dependence of exponent 1.96 (the inset in Fig. 6b). This square dependence underlines the occurrence of a two-photon excitation process.

3 Conclusions

Three N-monoalkylated diketopyrrolopyrrole (mDPP) derivatives, 3,6-bis(4-bromo-/chloro-/methyl-phenyl)-2-octyl-pyrrolo-[3,4-c]-pyrrole-1,4(2H,5H)-diones (named mDPP-Br/mDPP-Cl/ mDPP-Me), were synthesized from the commercially available or easy-prepared corresponding DPP derivatives and their oneand two-photon absorption and emission properties were investigated in the absence and presence of TBAF. Proton NMR titrations indicate that the addition of TBAF can induce the intermolecular proton transfer (IPT) between the hydrogen atom on the lactam N and the fluoride anion. Moreover, the electronically neutral (Ar-DPP-NH-Ar) and negatively charged (Ar-DPP-N⁻-Ar) species are all highly fluorescent ($\Phi = 0.32$ -0.61) and two-photon active (maximal δ is 108 GM without TBAF and 89 GM with TBAF), and the emission bands of negatively charged species are significantly red shifted relative to those of electronically neutral species. It is also observed that the emission bands of electronically neutral species are gradually decreased and those of negatively charged species are gradually increased with the addition of TBAF, which can be used as the ratiometric and fluorometric sensors for fluoride ions. Inspection of the one- and two-photon sensing properties reveals that these mDPP derivatives have high detection sensitivity to fluoride anions upon two-photon excitation, probably due to that the different excitation modes might involve different types of excited states among these mDPP derivatives, mDPP-Br and mDPP-Cl show better detection sensitivity to fluoride anions than mDPP-Me, implying that the substituent nature at the benzene rings of DPP could affect the two-photon absorption and sensing properties of mDPP derivatives. It is possible to further improve the molecular optical properties by a subtle manipulation of the substituent at the benzene ring of DPP derivatives, and which is underway in our laboratory.

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