Two-photon absorption enhancement induced by aggregation due to intermolecular hydrogen bonding in V-shaped 2-hydroxypyrimidine derivatives†

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The aggregation of V-shaped hydroxypyrimidine derivatives is formed through an intermolecular hydrogen bond in chloroform that cannot form a hydrogen bond with the solute, giving rise to a large enhancement of the two-photon absorption and two-photon induced fluorescence.

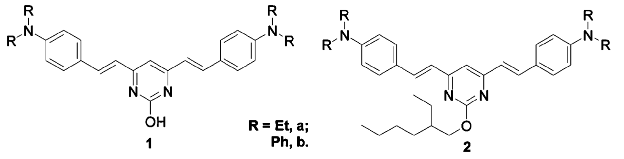
The promising applications of organic two-photon absorption (TPA) materials in optical limiting, two-photon laser scanning fluorescence imaging, microfabrication, 3-dimensional optical data storage, photodynamic therapy and so on,[1] have attracted considerable attention in the last decade and stimulated substantial research on structure–property relationships. Although it is still under exploration, thanks to the effort of scientists, some efficient molecular design strategies were put forward to provide guidelines for the development of materials with large TPA cross-sections, including the synthesis of D–π–D molecules with symmetric intramolecular charge transfer,[2] D–π–A molecules with asymmetric intramolecular charge transfer[3] and muti-dimensional molecules.[4] In these strategies, adjusting the action of molecular π-electron through changing the molecular substituents and/or structure is the key to obtain large TPA cross-section.

Molecular interaction is another efficient way to influence the action of molecular π-electron and might induce the large TPA cross-section.[5] In contrast to the research on molecular design strategy, little attention has been put into the influence of the molecular interaction on TPA property. Aggregation is one of the most common phenomenons of molecular interaction. It is important to understand the influence of aggregation on the molecular TPA property whether in research or in practical applications. Enhancement of TPA in molecular aggregates has been theoretically reported,[6] but experimental confirmation of aggregation-induced enhancement of TPA appeared only in the last two or three years. A strong enhancement of the TPA cross-section of porphyrin systems (symmetric[7] or asymmetric[8]) forming *J*-aggregates was reported, and an enhancement of the TPA cross-section in the *J*-aggregation of pseudoisocyanine was also observed in water by Belfield.[9] This enhancement is attributed to the electronic cooperative effect in both cases. Recently, Prasad has reported aggregation-enhanced fluorescence and two-photon absorption in nanoaggregates due to the hindering of molecular internal rotaion.[10] All these interesting results are of scientific significance and technical potential.

In this communication, we wish to report aggregation-induced enhancement of TPA and two-photon induced fluorescence (TPIF). To the best of our knowledge, this is the first example of TPA and TPIF enhancement induced by aggregation due to hydrogen bonding. The materials of interest in this work are V-shaped noncentrosymmetric D–π–A–π–D molecules, where D is an electron-donating, A an electron-accepting group and π a conjugating moiety (Scheme 1).

Both the UV-vis maximum absorption ($\lambda_{\max}^{\mathrm{ab}}$) of **1a** and **1b** (at a concentration of about 1×10^{-5} M) is red-shifted about 40 nm, respectively when the solvent of THF is replaced by $CHCl_3$. This implies a strong dependence of $\lambda_{\max}^{\mathrm{ab}}$ on the solvent in the solution of **1a** and **1b** (Fig. 1).

To check whether the shift is caused by solvatochromism,[11] we measure the UV-vis absorption of **1a** in a variety of solvents (at $\sim 1 \times 10^{-5}$ M). The relationship of $\lambda_{\max}^{\mathrm{ab}}$ of **1a** with the Snyder's polarity index of solvent is illustrated in Fig. 2, where two separate straight lines are drawn. In each line, $\lambda_{\max}^{\mathrm{ab}}$ increases with the increasing polarity of the solvents, implying the effect of solvatochromism. Obviously, however, the relationship between the polarity of solvent and $\lambda_{\max}^{\mathrm{ab}}$ is not monotonic. The longest $\lambda_{\max}^{\mathrm{ab}}$ does not appear in the most polar solvent (DMSO), but in CH_2Cl_2 and $CHCl_3$, and the shortest $\lambda_{\max}^{\mathrm{ab}}$ is not in CCl_4, which has the weakest polarity. So there must be another important factor to affect the $\lambda_{\max}^{\mathrm{ab}}$ of **1a** in different solvents. After careful examination of the solvent members in the individual line, it is found that the solvents can be divided to two groups. One group of solvents with higher ratio of $\lambda_{\max}^{\mathrm{ab}}$/polarity contains CCl_4, toluene, CH_2Cl_2 and $CHCl_3$, and all are not hydrogen bonding forming solvents, generally speaking. On the other hand, the other group with lower ratio of $\lambda_{\max}^{\mathrm{ab}}$/polarity consists of ether, THF, ethyl ester, acetone, DMF and DMSO, all of them are



Scheme 1 The molecular structure of **1a**, **1b**, **2a** and **2b**.

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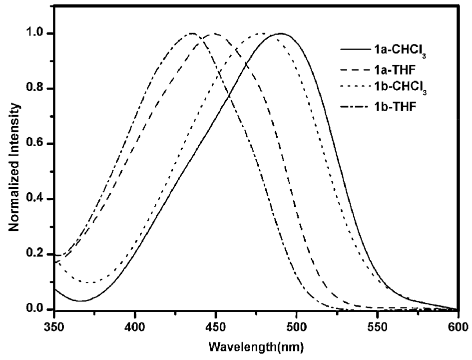


Fig. 1 The UV-vis absorption spectra of **1a** and **1b** in $CHCl_3$ and THF.

hydrogen bond acceptors and can form strong hydrogen bonds with hydroxyl in the compound **1a**.

Therefore, it seems reasonable to propose that in the first group of solvents, the solute **1a** form aggregates due to strong intermolecular hydrogen bonds so as to show the large red shift of λ^{ab}_{max}, while in the second group of solvents, the solvent can offer oxygen to form hydrogen bond with the hydroxyl of **1a** and prevent the solute self-aggregation (Scheme 2).

The proposal is confirmed by the NMR spectroscopy. The signals of the OH in the ^1H NMR spectra of **1a** (5.9×10^{-3} M) and **1b** (6.2×10^{-3} M) in $CDCl_3$ appears at 12.37 and 13.01 ppm, respectively. Both signals upfield shift continuously upon gradual dilution and appear at a position close to 10 ppm ($\sim 5.0 \times 10^{-4}$ M) (ESI†). This indicates that there are strong intermolecular hydrogen bonds in **1a** or **1b** in $CDCl_3$.[12] No obvious chemical shift of OH (at 10.78 ppm) is observed in the ^1H NMR spectra of **1a** in THF-d_8 when the concentration is diluted from 7.4×10^{-3} to 2.9×10^{-3} M, implying strong hydrogen bonds between THF and **1a**. The dependence of the UV-vis absorption on the concentration of **1a** in $CHCl_3$ also suggests that the intermolecular hydrogen bonding in aggregates is very strong since no obvious change of λ^{ab}_{max} is observed when the concentration is reduced gradually from 6.3×10^{-5} to 2.4×10^{-7} M. On the other hand, when THF is added gradually into the solution of **1a** in $CHCl_3$, the λ^{ab}_{max} is blue-shifted continuously, implying that the addition of THF could suppress the self-aggregation of **1a** (see ESI†). Both the results indicate that the self-aggregation exists in **1a** in $CHCl_3$ at the concentration of 6.3×10^{-5} M.

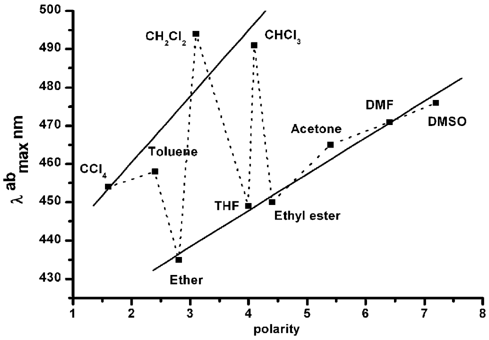
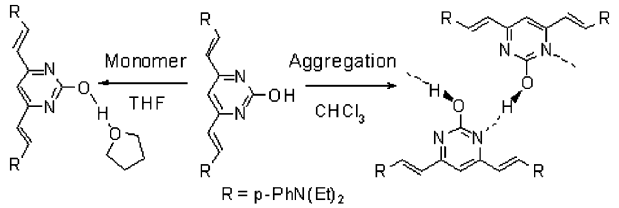


Fig. 2 The λ^{ab}_{max} of **1a** against the Snyder's polarity of the solvents.



Scheme 2 The hydrogen bonding of **1a** in $CHCl_3$ and THF.

To further examine the above explanation of the aggregation of **1a** and **1b**, we measured the UV-vis spectra of **2a** and **2b** in chloroform and THF, respectively, under the same conditions. Neither **2a** nor **2b** can form hydrogen bonds to each other or to an aprotic solvent since the hydroxyl has been replaced by alkoxyl. Unlike the large shift of λ^{ab}_{max} of **1a** and **1b** in different solvents, the λ^{ab}_{max} of **2a** and **2b** have a very small red shift when the solvent is changed from THF to chloroform. This confirms further that the intermolecular hydrogen bonding has an important influence on the UV-vis spectra of **1a** and **1b** in solution. It seems possible that the hydrogen bonding may have favored the formation of molecular π–π stacking among conjugated molecules, so as to promote the large difference of the UV-vis spectra of **1a** and **1b** in solution.

All the four compounds display good single-photon fluorescence in both $CHCl_3$ and THF. The single photon spectroscopic properties are listed in Table 1. The change trend of fluorescent maximum (λ^{em}_{max}) is similar to UV-vis absorption. The fluorescent quantum yields (Φ) of **1a** or **1b** in $CHCl_3$ and THF are almost the same, indicating that the effect of aggregation on the intensity of fluorescent emission is slight.

Two-photon absorption properties of the four compounds are measured between 720–930 nm in both $CHCl_3$ and THF by TPIF technique with a mode-locked Ti:sapphire laser (100 fs, 80 MHz).[13] The reason for choosing $CHCl_3$ and THF as solvents is that they have a similar polarity so as to exclude the effect of the solvent polarity on the TPA property.[5] All the TPA measurement of these compounds are performed with a concentration of about 1.0×10^{-4} M. The output intensity of TPIF of **1a** in $CHCl_3$ *vs.* the square of the input laser (850 nm) intensity has been calculated and the linear dependence indicates the occurrence of nonlinear absorption (See ESI†). The TPA spectra of the four compounds are shown in Fig. 3 and summarized in Table 2.

For **1a** and **1b**, the maximum TPA cross-section (σ) values are located at 820 nm in THF, but in $CHCl_3$ it appears at 920 nm for **1a** and 930 nm for **1b**. The large red shift is consistent with that observed in the UV-vis absorption spectra. However, for **2a** and **2b**, the maximum values are at 810 nm in $CHCl_3$ and at 800 nm in THF, which is also consistent with them having similar values of λ^{ab}_{max}. Each of the maximum σ values of **1a** and **1b** in $CHCl_3$ are more than two times larger than that in THF. However, for **2a** and **2b**, only a negligible change exists in different solvents, and the σ_{max} of **1a** and **1b** in $CHCl_3$ are threefold as large as those of **2a** and **2b** in $CHCl_3$ or THF. This indicates that the aggregation of **1a** and **1b** has enhanced their two-photon absorption largely.

Both **1a** and **1b** have two TPA bands in $CHCl_3$, but one in THF. Since the optimal wavelength used for two-photon excitation is roughly twice the linear absorption maximum wavelength,[2] the TPA band of **1a** and **1b** in $CHCl_3$ at a wavelength longer than 900 nm should be attributed to the lowest two-photon state of aggregates. The source of the band at less than 900 nm is complicated, although it appears at 850 nm the main contribution

Table 1 The single photon optical property of the four compounds

	λ_{max}^{ab}/nm		λ_{max}^{em}/nm		Φ^a	
	$CHCl_3$	THF	$CHCl_3$	THF	$CHCl_3$	THF
1a	491	449	585	550	0.30	0.27
1b	480	436	595	536	0.39	0.33
2a	435	431	515	516	0.45	0.46
2b	432	430	521	524	0.67	0.75

[a] Φ is the fluorescence quantum yield (reference: fluorescein pH = 11, Φ = 0.9).

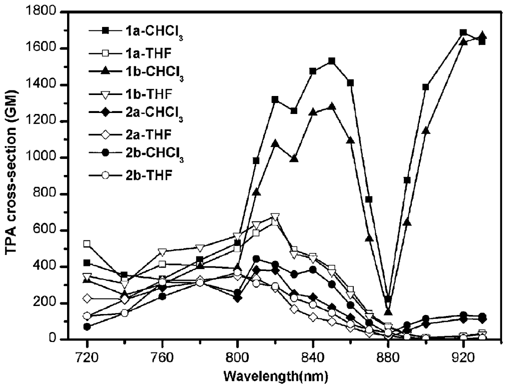


Fig. 3 The TPA spectra of the four compounds in $CHCl_3$ and THF.

Table 2 Two-photon absorption property of the four compounds

	$\lambda_{max}^{tp\ a}$/nm		σ_{max}/GM^b		δ_{max}/GM^c	
	$CHCl_3$	THF	$CHCl_3$	THF	$CHCl_3$	THF
1a	850, 920	820	1531, 1689	647	459, 507	175
1b	850, 930	820	1279, 1670	679	499, 651	224
2a	810	800	382	350	172	161
2b	810	800	443	369	297	277

[a] λ_{max} of the two-photon absorption spectra. [b] Two-photon absorption cross-section, 1 GM = 1 × 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$. [c] Two-photon excited action cross-section, $\delta = \sigma \times \Phi$.

to the band does not come from two-photon excited states of monomer since the monomer is rare in the solution of **1a** and **1b** in $CHCl_3$ due to the formation of aggregates induced by intermolecular strong hydrogen bonding. Furthermore, both the σ value of the band in **1a** and **1b** (in $CHCl_3$) are about twice as large as the σ_{max} of the monomer (in THF), however, the σ_{max} of **2a** and **2b**, which is a monomer in aprotic solvents, have no obvious enhancement in $CHCl_3$ in comparison to in THF. The results indicate that the occurrence of the band should not be attributed to the two-photon excited states of monomer. The band might come from either a higher energy two-photon excited state or a two-photon resonance state as mentioned in other aggregates.[7,14] A further study is needed to deepen the understanding.

It is notable that the aggregation of **1a** and **1b** has induced large enhancement of the σ value, but has little effect on the fluorescence quantum yield. This means that aggregation induces enhancement of TPIF of **1a** and **1b**. The enhancement of fluorescence is the result of the augmentation of excited molecules at the same excited condition, since the σ value in aggregates is larger than that in monomers at wavelengths longer than 800 nm. From Table 2, it can be found that the maximum of the two-photon excited action cross-section (δ_{max}) increases by about 3-fold in aggregates in comparison with the monomer.

In conclusion, the aggregation of V-shaped molecules containing 2-hydroxypyrimidine has been formed due to the intermolecular hydrogen bonding in the solvents that cannot form hydrogen bonding with the solute as evidenced by UV-vis absorption and ^{1}H NMR. And an aggreagation-enhanced two-photon absorption has been observed in $CHCl_3$. As a result, an emission enhancement of two-photon excited fluorescence arises. This provides some important and new informations for potential application based on two-photon absorption.

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