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Y-shaped two-photon absorbing molecules with an imidazole–thiazole core†

Ke Feng,[a] Leonardo De Boni,[b] Lino Misoguti,[b] C. R. Mendonça,[b] Michael Meador,[c] Fu-Lian Hsu[d] and Xiu R. Bu*[a]

[a] *Department of Chemistry and NASA Center for High Performance Polymers and Composites, Atlanta, Georgia 30314, USA. E-mail: xbu@cau.edu*
[b] *Departamento de Física e Ciência dos Materiais, Instituto de Física de São Carlos, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil. E-mail: crmendon@.if.sc.usp.br*
[c] *Polymer Branch, NASA Glenn Research Center, Cleveland, OH 44135, USA*
[d] *US Army Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010, USA*

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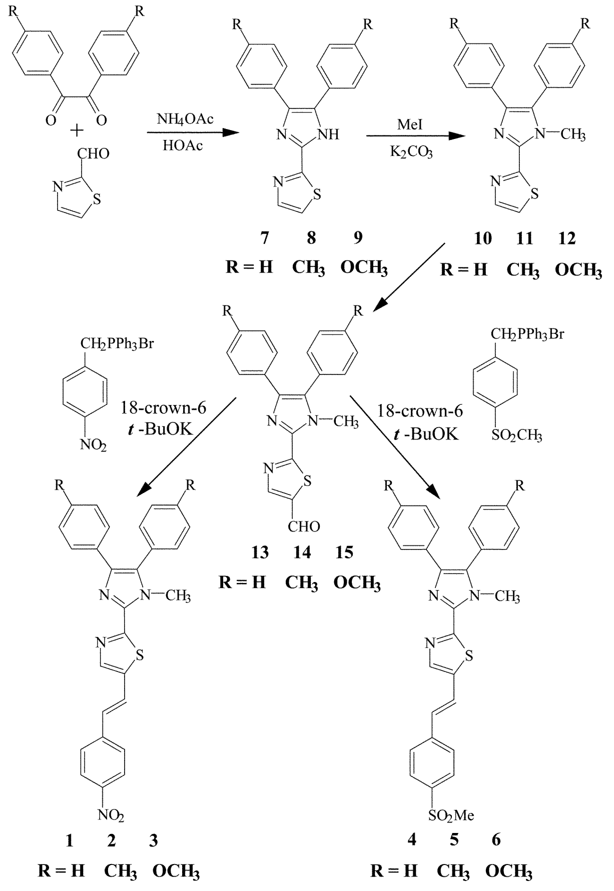
Two new classes of two-photon absorbing Y-shaped molecules have been developed to possess an imidazole–thiazole core and a stilbene-type conjugation pathway with either nitro or sulfonyl as terminal electron-accepting group.

The emergence of applications of two-photon technology to up-converted lasing, optical power limiting, photodynamic therapy and generation of singlet oxygen, three-dimensional micro-fabrication and data storage, and three-dimensional fluorescence microscopy,[1] has drawn an increasing interest in the design and development of two-photon absorbing molecules with large nonlinear absorptivity to generate a high-energy excited state with relatively low laser energy. The new structure–property correlation is being sought to establish guidance for molecular design since the ability of organic molecules to simultaneously absorb two photons to reach the excited state depends on molecular structures. Several strategies[2,3] based on schemes such as D–π–D, D–π–A–π–D, and A–π–D–π–A (D: electron donating group, A: electron accepting group, and π: conjugated pathway) have been found to enhance the δ value, the two-photon absorptivity. The common structural features in these designs are (1) molecular symmetry and (2) the use of amine related groups such as diphenylamine and carbazole as D components. Other molecular architectures for large two-photon absorption include branched multi-conjugated systems furnished with D and/or A components,[4] dendrimers with terminal D components[5] and fused aromatic systems with planar π-cores such as fluorene,[6] dithienothiophene,[7] and perylene.[8] We here report two novel classes of Y-shaped molecules with large two-photon absorptivities.

Two new series of chromophores **1–3** and **4–6** were synthesized *via* intermediates **13–15**, which were obtained by a procedure starting with the condensation[9,10] of benzil derivatives with 2-formylthiazole to afford **7–9**. The methylation of **7–9** with iodomethane in the presence of a base gave **10–12**, which were treated with *n*-butyl lithium, followed by the addition of DMF to produce **13–15** (Scheme 1). The Wittig reactions of 4-nitrobenzyl triphenylphosphine bromide with **13–15** led to the formation of **1–3** while the reactions with 4-methylsulfonylbenzyl triphenylphosphine bromide yielded **4–6**. Chromophores **1–3** absorb with $\lambda_{\max}$ in the range of 422–433 nm, **4–6** in the range of 398–410 nm.

Nonlinear optical measurements for two-photon absorption properties of **1–6** were carried out with the Z-scan technique, which indicates two distinct absorptive nonlinear processes: the two-photon absorption (2PA), and the saturable absorption (SA). For wavelengths between the resonant and the onset of nonresonant regions, these two processes are competing. The SA process at 500 nm is shown in gray and the 2PA process signature at 600 nm is shown in black (Fig. 1). For wavelengths in the nonresonant region, the 2PA process is unique.



Scheme 1 Structures of two new series of chromophores.

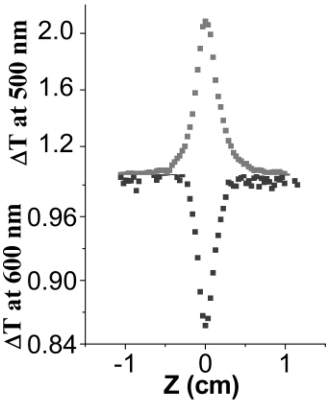


Fig. 1 Z-scan signatures at different wavelengths from **4**.

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† Electronic supplementary information (ESI) available: synthesis and characterization of **1–6**, and 2PA measurement. See http://www.rsc.org/suppdata/cc/b4/b402019g/

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The 2PA spectra profiles in the range of 600–1000 nm for **1–3**, and 550–1000 nm for **4–6** are shown in Fig. 2. The peaks around 700 nm are listed in Table 1 along with additional peaks around 600–640 nm. The increase in the 2PA intensity below 700 nm is due to resonance enhancement of the optical nonlinearity near the one photon transition, in agreement with the resonant denominator in the sum-over states model.[11] Table 1 displays the concentration and the wavelength peak with their correspondent δ values (peak) obtained in the nonresonant region for the six solutions.

The δ values obtained for the 2PA cross-sections indicate that all compounds exhibit a high 2PA process far from the resonance. The chromophore **6** gives 1700 GM at 760 nm, which is comparable to some of the leading chromophores:[12] for example, the bis donor D–π–D compound:[3] 1420 GM; dendrimers with D-end:[5] 400–800 GM, dithienothiophene core-based compounds:[7] 130–1900 GM; perylene core-based compounds: 84–1200 GM;[8] and multi-branched conjugates: 1390–2620 GM.[4]

Sulfonyl-based chromophores turn out to be more efficient for 2PA, in nonresonant conditions, compared to nitro-based ones. A close examination of δ values from 2PA $\lambda_{\max} > 700$ nm reveals that the resultant difference from these two series is significant in the following: several systems examined so far have demonstrated[6] that a stronger acceptor will lead to the δ enhancement. That is the reason why the nitro group is often used.[6] Based on the Hammett constant scheme for *para*-substitution, the σ_p is 0.81 for the NO_2 group and 0.73 for the SO_2Me group,[13] respectively, indicating that the nitro group is a stronger electron-accepting group. However, the present chromophores show the opposite trend, with sulfonyl group-based chromophores giving higher δ values than nitro group-based ones do. For example, the value of **6** (R = OMe) is 1.6 times that of **3** while the value of **5** (R = Me) is 2.2 times that of **2**.

It is also interesting that the present chromophores achieve large 2PA without the use of amine-based donor groups such as NMe_2 (for R). Methoxy (R = OMe) is the strongest donor used for these two series.

The fact that the large δ values from the present chromophores are highly comparable to those from well-studied D–π–D systems is remarkably significant because the current structural architecture is unsymmetric. We have examined the molecular geometry to determine the conjugation pathway of this unsymmetric system. Two phenyl rings have different twists from imidazole, and the conjugation from one phenyl ring is better than the other with imidazole.[14] The molecular geometry optimized by DF 6-31G* shows that one phenyl (at the 4-position) is only twisted 26–29° from the imidazole ring while the other (at the 5-position) is twisted 53–57°, suggesting that one donating group primarily contributes to the push–pull structure through better conjugation due to less twist between two adjacent aromatic rings. For the rest of the chromophores, namely from imidazole to thiazole and all the way to the accepting group, the geometry is relatively planar. For instance, the twists of the two phenyls from imidazole in **6** are 28.82° and 53.59°, respectively. Imidazole and thiazole are almost co-planar, with a deviation of only 1.89°. The vinyl moiety is also positioned well with two adjacent aromatic rings, thiazole and phenyl, with deviations of 1.11° and 3.87°, respectively. Accordingly, the HOMO and LUMO mainly reside on the following pathway: phenyl with accepting group, vinyl, thiazole, imidazole, and the phenyl at the 4-position (Fig. 3). Both series, regardless of the type of electron-accepting groups, possess the same conjugation pathway. This conjugation pathway is responsible for the increase in permanent dipole moments from H → OMe for R (nitro group series: **1**: 8.52; **2**: 9.22; **3**: 11.0 Debye; sulfonyl group series: **4**: 7.30; **5**: 8.41; and **6**: 10.06 Debye). The charge transfer from donor to acceptor along this pathway leads to an increase in the δ values from H → OMe (R) in both series of chromophores. The contribution from the phenyl at the 5-position is minimal due to a large twist from the imidazole ring. In addition, the higher δ values from the sulfonyl-based chromophores may be ascribed to larger transition dipole moments M_{ge} and M_{ee}.[3]

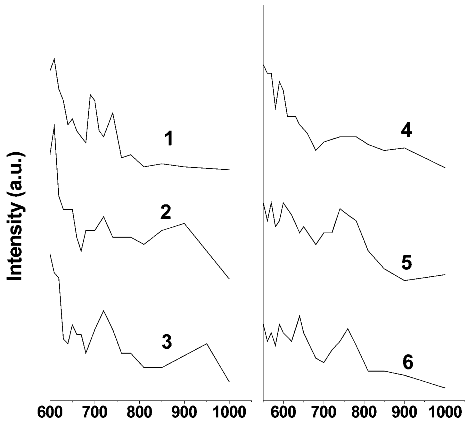

Fig. 2 Two-photon absorption.

Table 1 2PA cross-section coefficients

	[C][a]	2PA $\lambda_{\max}$ (nm)	δ (GM)[b]
1	2.3	610, 690	2100, 1500
2	4.8	610, 720	1300, 650
3	6.6	600, 720	1450, 1050
4	5.3	590, 740	1100, 460
5	5.9	600, 740	1500, 1400
6	5.4	640, 760	2000, 1700

[a] 10^{17} molecules/cm^3. [b] 1 GM = 10^{-50} cm^4 s photon^{-1}.

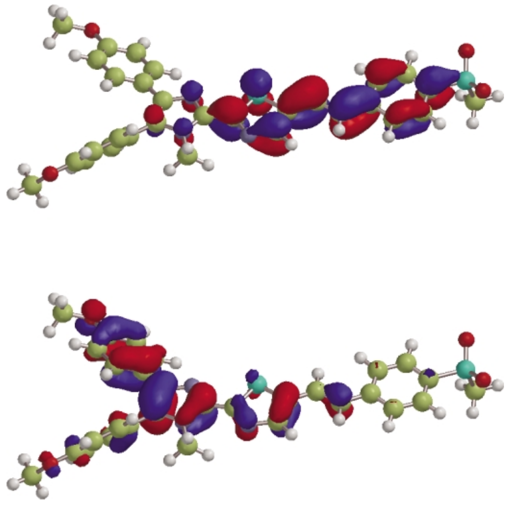

Fig. 3 The LUMO (top) and HOMO (bottom) of **6**.

In summary, we have developed two new classes of Y-shaped molecules that possess large two-photon absorptivity. The imidazole–thiazole core provides a planar core geometry and the minimal deviations between the two rings are due to the fact that thiazole does not possess any adjacent hydrogen which could potentially interact with imidazole and cause a twist.[15] One series of chromophores has sulfonyl as an electron-accepting group while the other has nitro. The chromophores that possess the sulfonyl group exhibit larger δ values than those with the nitro group.

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