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Synthesis and two-photon absorption property of phenylacetylene macrocycles☆

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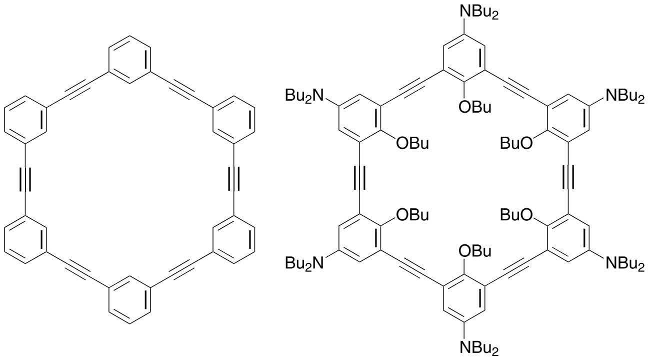
Abstract—The first synthesis of phenylacetylene macrocycle with large two-photon absorption cross section is reported. © 2003 Elsevier Science Ltd. All rights reserved.

Phenylacetylene macrocycles (PAMs) have been extensively investigated because of their potential as functional materials. Since the first synthesis of unsubstituted PAM (Fig. 1),[1] a variety of PAMs,[2] PAM derivatives having a larger cavity,[3] PAM analogues incorporating chiral[*c*]phenathrene units,[4] PAMs bearing *endo*-annular methoxy groups,[5] and *m*-diethynylbenzene macrocycles (DBMs)[6] have been synthesized and their self-association in solution,[6,7] organization to porous molecular crystals,[8] liquid crystals,[9] monolayer surfaces,[10] organization in solution,[11] in condensed phase,[12] and on the solid surface,[11] as well as guest binding abilities[5,13] were studied. The results show that these properties based on the nonbonding interactions can in principle be fine-tuned by modifying the size and shape of the macrocycles and nature of the functional groups attached to the periphery and interior of the macrocyclic framework.



PAM **1**

Figure 1. Structures of PAM and **1**.

We envisioned that the shape persistent symmetrical structures of PAMs might be a promising candidate for two-photon materials. Recently, substantial research efforts have been directed to develop organic materials with large two-photon absorption (TPA) cross sections for possible applications in optical power limiting,[14] two-photon upconversion lasing,[15] two-photon fluorescence excitation microscopy,[16] three dimensional optical data storage,[17] and photodynamic therapy.[18] Synthesis of efficient TPA materials is important because such molecules would exhibit greater sensitivity in the two-photon activated processes and allow lower laser intensities to be used for the excitation, which would in turn reduce the probability of optical damage. A variety of compounds including donor–bridge–acceptor (D–π–A) dipoles,[19] donor–bridge–donor (D–π–D) quadrupoles,[20] multi-branched compounds,[21] dendrimers,[22] and octupoles[23] have been synthesized and their structure–property relationship established.[19–24] However, there is still a need to develop reliable design strategy for the development of efficient TPA chromophore.

In this connection, we have initiated a research program aimed at establishing the structure–TPA property relationship of PAMs as a new class of TPA chromophores. This compound offers several potential advantages as TPA materials. It is well established that more rigid fluorophores are more fluorescent.[25] Hence, PAM should be strongly fluorescent because three

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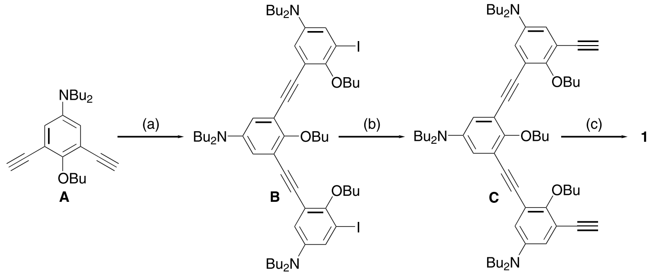
molecules of diphenyacetylene (DPA) are incorporated into a cyclic structure, although the fluorescence quantum yield of DPA is very small.[26] Therefore, if it is possible to excite this molecule by a two-photon process, one may obtain a strong two-photon induced fluorescence. Moreover, since PAM is an octupolar molecule, the one- and two-photon allowed states are expected to be the same. This would make it possible to tune the two-photon excitation wavelength by adjusting the one-photon absorption maximum $\lambda^{(1)}_{max}$. Furthermore, PAMs can be developed for a variety of applications by introducing appropriate functional groups at the phenyl groups.

As a first step toward this goal, we have synthesized a PAM derivative **1** containing butoxy and dibutylamino groups at the 2- and 5-positions of the phenyl groups, respectively, and studied its one- and two-photon properties (Fig. 1). Both groups are introduced as the donor and to increase the solubility. The synthesis of **1** is summarized in Scheme 1.



Scheme 1. *Reagents and conditions*: (a) 1-butoxy-4-dibutylamino-2,6-diiodobenzene (2 equiv.), $PdCl_2$ $(PPh_3)_2$, CuI, Et_3N/THF (1:3), rt, 18 h, 25%; (b) (i) TMSacetylene, $PdCl_2$ $(PPh_3)_2$, CuI, Et_3N/THF (1:2), rt, 12 h, 80–95%, (ii) 1 M KOH, MeOH/THF (1:10), rt, 1 h, 100%; (c) **B**, $PdCl_2$ $(PPh_3)_2$, CuI, Et_3N, rt, 48 h, 15%.

Intermediate **A** was prepared in a quantitative yield by Sonogashira coupling between 1-butoxy-4-dibutylamino-2,6-diiodobenzene and TMSacetylene followed by the removal of trimethylsilyl group with OH^-. **B** was obtained in 25% yield by the coupling of 1-butoxy-4-dibutylamino-2,6-diiodobenzene and **A** in 2:1 ratio. Reaction of **B** and TMSacetylene followed by deprotection with OH^- afforded **C** in 80% yield. The PAM derivative **1** was obtained in 15% yield by the coupling between **B** and **C**.[27] Although the overall yield is low, the target compound could be synthesized without much problem.

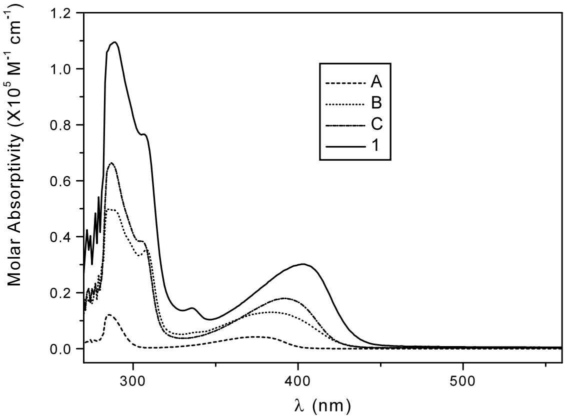


Figure 2. Molar absorptivity spectra of **A**–**1** in toluene.

Figure 2 shows the molar absorptivity spectra of **A**–**1**. The short wavelength absorption maxima of these compounds are similar to those of DPA and PAM, whereas the long-wavelength bands show large red shifts by approximately 70–100 nm compared to those of the latter (Table 1). In addition, the long-wavelength absorption maxima for **A**–**1** increase gradually with the conjugation length. This is in contrast to PAM whose $\lambda^{(1)}_{max}$ is almost the same as DPA, despite that the former is built up by three units of the latter. Thus, the large red shift in the lower energy band and the gradual increase in $\lambda^{(1)}_{max}$with the conjugation length can be attributed entirely to the donor groups (Bu_2N and BuO). Moreover, the $\lambda^{(1)}_{max}$ values are relatively insensi-

Table 1. One-photon properties of DPA, PAM, and **A**–**1**

Compds	Solvent	$\lambda^{(1)}_{max}$ [a]	λ^{fl}_{max} [b]	$\Delta\nu_{st}$ [c]	Φ [d]
DPA[e]	MeCN	285, 304	298, 302	−220	4×10^{-3}
PAM[f]	THF	284.5, 302			
A	Toluene	291, 375	423	3026	0.30
	DMF	291, 375	430	3411	
B	Toluene	288, 382	454	4152	0.025
	DMF	288, 387	468	4472	
C	Toluene	292, 392	450	3288	0.52
	DMF	292, 396	467	3839	
1	Toluene	289, 403	466	3354	0.25
	DMF	289, 413	486	3637	

[a] λ_{max} of the one-photon absorption spectra in nm.

[b] λ_{max} of the one-photon emission spectra in nm.

[c] Stokes shift in cm^{-1}, $\Delta\nu_{st}=\nu_{abs}-\nu_{fl}$.

[d] Fluorescence quantum yield.

[e] Ref. 26.

[f] Ref. 1.

tive to the solvent polarity. This suggests that the ground state and Franck–Condon singlet state have similar dipole moments. Finally, the molar absorptivity increases in the order **A**<**B**<**C**<**1**, probably because of the increased concentration of the phenylacetylene moities.

Fluorescence spectra of **A**–**1** are broad and show $\lambda^{\mathrm{fl}}_{\mathrm{max}}$ at 423–466 nm (Fig. 3). The Stokes shifts calculated by the difference between the long-wavelength absorption maxima and $\lambda^{\mathrm{fl}}_{\mathrm{max}}$ are in the range of 3026–4152 cm^{-1}, which is much larger than that of DPA. This result indicates that, unlike DPA whose ground- and excited-state structures are similar, there is a significant difference between them in **A**–**1**. Moreover, $\lambda^{\mathrm{fl}}_{\mathrm{max}}$ are appreciably red-shifted in a more polar solvent. This indicates that the excited state should have significant polar character, providing supporting evidence for the above conclusion. Except for **B** whose fluorescence quantum yield is low because of the heavy atom effect, the quantum yields of **A**–**1** are much larger than DPA (Table 1). DPA is known to be an anomalous fluorophore, wherein excitation occurs to and emission occurs from S_2, and exhibits very low quantum yield because of the existence of the dominant nonradiative decay pathway, i.e. the internal conversion from S_2 to S_1 followed by a rapid intersystem conversion from S_1 to T_1.[26] The much higher quantum yields of **A**–**1** reveal that such pathway does not exist in these molecules. In addition, the quantum yield of **1** is smaller than those of **A** and **C**, despite the increased rigidity. The origin of this dichotomy is not clear at present.

The two-photon cross section δ was measured by using the two-photon-induced fluorescence measurement technique with the following equation:

$$\delta = \frac{S_s \Phi_r \phi_r c_r}{S_r \Phi_s \phi_s c_s} \delta_r$$

where the subscripts s and r stand for the sample and reference molecules.[20c] The intensity of the signal collected by a PMT detector was denoted as *S*. Φ is the fluorescence quantum yield. ϕ is the overall fluorescence collection efficiency of the experimental apparatus. The number density of the molecules in solution was denoted as *c*. δ_r is the TPA cross section of the reference molecule.

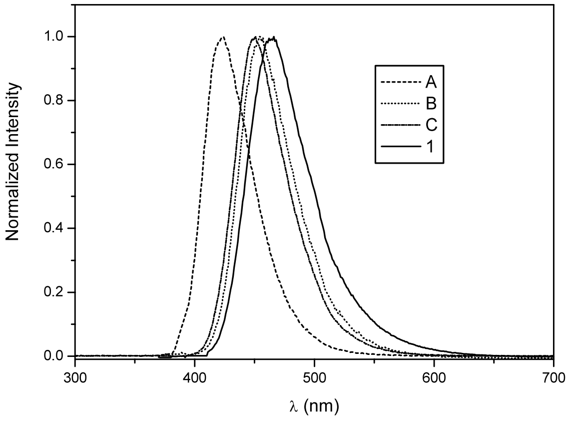


Figure 3. Normalized one-photon fluorescence spectra of **A**–**1** in toluene.

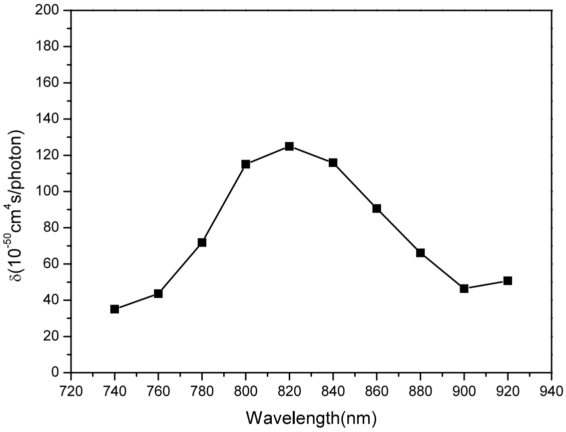


Figure 4. Two-photon excitation spectrum of **1** in toluene.

Figure 4 shows the two-photon-induced fluorescence (TPF) excitation spectrum of **1**. The shape of the spectrum is similar to the long wavelength peak in the absorption spectrum shown in Figure 2, except that the wavelength is doubled, $\lambda^{(1)}_{\mathrm{max}} = \lambda^{(2)}_{\mathrm{max}}/2$. This indicates that the two-photon allowed state of **1** is close to the lower energy one-photon allowed state. Also, the λ_{max} of the two-photon absorption spectrum is 820 nm. This turns out to be very important for practical applications, because most of the TPF microscopy uses a visible beam with a wavelength of 800 nm. Finally, the maximum value of the two-photon absorption cross section (δ_{max}) is 125 GM, which is three times larger than that of fluoroscein and comparable to Rhodamine B.[28] This compound may eventually find a useful application as TPA chromophore.

In conclusion, we have synthesized PAM derivative **1** containing Bu_2N and BuO as the donor. The donors increase the long-wavelength absorption maxima and the Stokes shift. Also, the Stokes shift is larger in a more polar solvent, indicating a significant charge transfer in the excited state. The δ_{max} of **1** is 125 GM at $\lambda^{(2)}_{\mathrm{max}} = 820$ nm. We are currently synthesizing more efficient PAMs with large TPA cross sections.

Acknowledgements

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