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Utilizing formation of dye aggregates with aggregation-induced emission characteristics for enhancement of two-photon absorption

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Femtosecond Z-scan measurements of aggregates of a quadrupolar D- π -D dye, 9,10-bis(*N*-hexylcarbazol-2-yl-vinyl-2)anthracene (BHCVA), provide direct evidence that aggregation of this AIE (aggregation-induced emission) chromophore leads to a sizeable enhancement of the intrinsic two-photon absorption cross section. Aggregation-induced improvement of nonlinear response is explained by theoretical analysis of electronic structure and geometrical parameters of aggregates.

Over the past two decades numerous synthetic strategies for designing nonlinear chromophores with high two-photon absorption (TPA) efficiency have been developed, focusing on boosting the electron density delocalization within a molecule and creating dipolar or multipolar charge distribution.¹ Beyond the molecular level, it has also been demonstrated that the TPA strength can be increased by effects that arise from through-space interactions between π -electron densities of molecules or molecular fragments, sometimes referred to as "cooperative effects".²

Indeed, increase of the TPA cross section (σ_2) upon dendrimer formation³ or molecule aggregation⁴ has been postulated in several reports, including huge cross sections in protein aggregates like amyloids⁵ and silk,⁶ as well as aggregates of relatively small molecules (i.e. sulfonated porphyrins and Thioflavine T).⁷ Notably, cooperative effects elicited by the close proximity of ligand molecules are also considered to be responsible for strong TPA response of solid-state materials

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Electronic Supplementary Information (ESI) available: BHCVA synthesis and characterization, experimental details of NLO studies and additional discussions, details of theoretical calculations. See DOI: 10.1039/x0xx00000x

such as Metal-Organic Frameworks (MOFs).^{8,9}

The formation of aggregates of some specific classes of compounds (called AIE-gens derivatives of tetraphenylethene, anthracene, phenylsiloles to name only a few of them¹⁰) leads to the interesting phenomenon of aggregation-induced emission (AIE)¹¹⁻¹⁴ which consists in, sometimes dramatic, increase of the quantum efficiency, φ , of luminescence of a chromophore.¹⁵⁻¹⁷ From the point of view of applications of TPA chromophores, especially related to imaging, the AIE effect is very beneficial, as it enhances the brightness of the two-photon induced luminescence ($\varphi \sigma_2$) which is of importance for bioimaging of cells or tissues where molecular crowding often leads to a spontaneous aggregation.^{18, 19}

While the increase of fluorescence quantum yield of molecules featuring the AIE effect is a well-proven matter and has been exploited in TPEF (two-photon excited fluorescence) studies ²⁰⁻²² a nontrivial point is whether the observed enhancement of the two-photon induced emission is due solely to the increase of the quantum yield, or if the TPA process itself (that is, increase of the intrinsic TPA cross section) may also contribute to the observed effects.

The above issue has been noted,²³ but still lacks direct experimental evidence. We present here a set of femtosecond Z-scan results, corroborated by computer simulations clearly demonstrating that aggregation of an AIE compound significantly boosts (over two-fold) the *intrinsic* TPA cross section.



Fig. 1. The structure of BHCVA. Bonds in bold indicate the dihedral angle affected by aggregation, as discussed in further sections.

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As a model compound for our studies we have designed and prepared a quadrupolar donor- π -donor AIE molecule (**BHCVA**, Fig. 1) and, using different ratios of solvent and non-solvent, we have induced aggregates formation. Synthetic procedures, NMR characterization, and discussion of mechano-, vapo- and termochromic properties are provided in the ESI, Figs. S1 – S12.

Confirmation of AIE nature of BHCVA was performed in THF:water mixtures at low compound concentration (see ESI, Fig. S14). As it was expected, in pure THF and in mixtures with low contribution of water almost no fluorescence was observed. For 50% (v/v) content of water BHCVA started to crystallize, which was deduced from emission peak at 529 nm, being the same as for the bulk BHCVA. Further experiments were performed in highly concentrated BHCVA solutions in THF and chloroform (2.74 mM), required for NLO studies (see below). High concentration already promotes aggregate formation, even in pure solvents, which is observed in absorption spectrum. However, in order to obtain progress in aggregation and at the same time avoiding bulk crystallization, for those systems acetone was used as a poor solvent. The determined thresholds above which bulk crystallization of BHCVA occurs in chloroform/acetone and THF/acetone mixtures are 20% and 50% (v/v) of acetone, respectively.

Subsequently, we explored the two-photon absorption using the well-established Z-scan technique in wavelength range 625-900 nm, employing low repetition rate (1 kHz), ~130 femtosecond laser pulses to minimize contributions from processes other than instantaneous nonlinear absorption. A crucial advantage of this method (over TPEF measurement) is that it directly provides information on the strength of twophoton absorption properties, since the results do not depend on the quantum yield of fluorescence.²⁴ Details on the experimental setup and sample preparation are given in the ESI. Additional information about non-radiative processes was provided by pump-probe experiments.

Fig. 2 presents two-photon absorption spectra of **BHCVA** in six different solvent/non-solvent mixtures. We found the most significant effects near the 675 nm wavelength. Firstly, sizeable enhancement of two-photon properties for **BHCVA** is observed when the solvent is changed from pure chloroform to mixtures with acetone. Secondly, 2.5-fold enhancement is observed (from 164 GM to 408 GM) in a solution with 10% of acetone, and further 1.25-fold increase up to 503 GM, for 20% acetone content. For the pure THF and THF solution with 40% of acetone the two-photon spectra are almost the same (peaking around 370 GM at 700 nm). However, nearly two-fold enhancement of TPA response to 720 GM is observed when the acetone content is equal to 50%.

It is a known fact that two-photon response can scale in various ways with the size of the conjugated scaffold, thus meaningful interpretation and comparison of the two-photon cross sections, especially between different types of compounds, necessitates the use of figures of merit such as the cross section normalized by molar mass (σ_2 /M). Here, we take as an example **BHCVA** aggregates in 50% THF - 50% acetone mixture; σ_2 /M value at 700 nm is equal to 0.99

 $GM \cdot mol \cdot g^{-1}$, which falls within the range of good organic and organometallic TPA chromophores.²⁵⁻²⁷

We have also studied the wavelength region corresponding to three-photon absorption of **BHCVA** (1100-1350 nm). Aggregates in chloroform do not exhibit clean three-photon absorption signatures. Instead, open-aperture Z-scan traces clearly showed presence



Fig. 2. Two-photon cross-section of BHCVA a) in solution of increasing volume ratio of acetone in chloroform plotted with one-photon absorption of diluted BHCVA in chloroform (solid gray line); b) in solution of increasing volume ratio of acetone in THF plotted with one-photon absorption of diluted BHCVA in THF (solid gray line). Full lines, connecting Z-scan-derived experimental points are drawn just to guide the eyes.

of photochemical processes that occurred at the focal point of the laser beam (ESI, Fig. S15). This was confirmed in a separate experiment, in which we irradiated the chloroform solution of **BHCVA** with 800 nm laser light for 3 hours. The photodegradation was evident, as judged from ¹H NMR spectroscopy (ESI, Fig. S16). Photochemical reactions occurring in the focal point seem to be main reason why no clear comment on possibility of enhancement of the three-photon response can be provided (ESI, Fig. S17).

Since the formation of aggregates is clearly found to increase the TPA cross section, one needs to identify the possible structural and electronic origin of such an enhancement.

Two alternate mechanisms may be considered. The first notion points to the fact that aggregation causes molecules



578 nm 614 nm Wavelength [nm]

Fig. 3. Schematic representation of changes in electronic structure upon type A dimer formation. Vertical bars represent relative changes in the two-photon absorption cross section. Orbitals on the left (right) side correspond to $4A_g \leftarrow 1A_g$ ($9A_g \leftarrow 1A_g$) large-intensity two-photon transitions. Dashed lines on both diagrams depict photon energy.

possessing normally rotatable fragments (such as single bond connected to vinylic carbons in **BHCVA**, Fig. 1) to be planarized, which results in better π -electron delocalization throughout the aromatic skeleton; the second approach focuses on intermolecular interactions between neighbouring molecules.

To assess which of these factors are likely to be of importance, we performed electronic structure calculations employing the density functional theory for monomer, and set of aggregation models (two dimers and two trimers), assuming C_i symmetry point group. The details of these calculations are presented in the ESI, here we briefly discuss the most important findings.

There is no straightforward experimental method that could provide the precise structure of nanoaggregates, which makes electronic structure calculations of those systems challenging. For this reason, we assume that due to the presence of aromatic rings and significant dispersion interactions, the studied molecule aggregates and the anthracene central moieties form parallel stacks. Two scenarios of aggregation are drawn on the above assumption. In the aggregation model of type A the dimer and trimer ensembles tend to glide along long axis of **BHCVA** molecule, while in type B aggregation the **BHCVA** molecules form stacks, significantly glided along short axis (that is, along anthracene fragment) of **BHCVA**. Note that the latter type of aggregation model is proposed on the basis of analysis of crystallographic motifs of molecules structurally related to **BHCVA** (see ESI for discussion).

In the first step, we have compared the TPA transition moments calculated for monomer and aggregate structures of type A and B. A comparison of values collected in Tables S18-S20, ESI, shows that type A aggregation affords ca. 50% and 105% higher two-photon absorption cross section for dimer and trimer, respectively, than that for the monomer. Interestingly, type B aggregation results in negligible enhancement of TPA cross section (maximally 10% for dimer, see Tables S24 and S25, ESI). In light of experimental results, which clearly show that the aggregation yields even 250% rise

of the TPA cross section, we suggest that type A aggregation is a much more probable scenario.²⁸ Therefore, further comment will be provided mainly for this model of aggregation.

In single BHCVA molecule the dihedral angle between the plane of vinylic bond and the plane of anthracene fragment, denoted as ϕ in Fig. 1, is equal to 127.4°. Centrosymmetric BHCVA dimer and trimer aggregation models of type A show strong tendency for planarization of vinyl bond-anthracene region. Indeed, for dimer two distinct ϕ angles, equal to 128.4° and 138.6°, can be found while for trimer the planarization is even more pronounced since three ϕ angles were determined (134.6°, 144.4°, 145.3°). By contrast, aggregation models of type B reveal fairly changed ϕ angles with respect to monomer (127.1°, 134.8° for dimer, 125.3°, 127.2°, 133.3° for trimer). In the ESI, Fig. S18, are drawn all **BHCVA** models with indicated ϕ angles. Those results suggest that molecular aggregation of type A leads to flattening of the aromatic skeleton, which appears to be directly connected to the elevated TPA response. Next, we focused on the electronic origin of observed TPA enhancement. The aggregation leads to changes in electronic structure, i.e. there is a 35 nm red shift in the excitation wavelength corresponding to the large-intensity one-photon transition to the 1A₁₁ state and this is in line with the experimental finding. The results of calculations also reveal that the most intense two-photon transitions are $4A_g \leftarrow 1A_g$ (578 nm, monomer) and $9A_g \leftarrow 1A_g$ (614 nm, dimer). The TPA cross sections associated with these two transitions are at least one order of magnitude larger than the values for any other symmetry-allowed transitions (see ESI).

Fig. 3 shows the nature of these TPA transitions for monomer and dimer of type A. There is a symmetrical electron density shift from carbazole moieties to anthracene central unit (and reverse). It is important to note that in the case of the dimer one observes ca. 50% increase in TPA cross section in comparison with the monomer. This suggests that aggregation gives rise to very large TPA in the spectral region above 600 nm. In order to gain an insight into aggregation-induced

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DOI: 10.1039/C7TC05509A Journal Name

increase in TPA intensity we performed an analysis of electronic structure parameters (transition moments and excitation energies). It turns out that the change in the transition energy to the 1A_u state upon dimer formation is the most important factor responsible for increase in TPA response.

We have also attempted to apply an aggregation model of higher complexity. To this end, we calculated absorption features of aggregate consisting of three stacked BHCVA molecules. The maximum of one-photon excitation wavelength of trimer is shifted by additional 16 nm (with respect to the dimer). Moreover, calculation of two-photon properties shows that there are a few intense two-photon transitions occurring in close proximity to the most intense one, which is $12A_g \leftarrow 1A_g$. Fig. 3 shows the energy diagrams corresponding to two-photon $4A_g \leftarrow 1A_g$ (monomer) and $9A_g$ \leftarrow 1A_g (dimer) transitions. As seen, in the case of the dimer the detuning factor (the difference between $1A_u \leftarrow 1A_g$ transition energy and the photon energy) is much smaller than that for the monomer which, according to quantum mechanical sumover-states expressions, results in the increase of two-photon absorption probability. Together they contribute to further increase of the TPA cross section (see ESI).

Those findings clearly indicate that the observed increase of two-photon response is related to mixed through-space (stacking of molecules) and predominantly through-bond (planarization of π -skeleton) enhancement mechanisms, which proceed due to the formation of aggregates.

Influence of aggregation degree on excited state was also tracked with transient absorption and fluorescence decay. Similar to the Z-scan experiments, the time-resolved emission and absorption were studied in solvent/non-solvent mixtures at high concentration of BHCVA (2.74 mM).

Both the transient absorption (TA) and fluorescence decay results show that the aggregation can significantly influence the photophysical parameters of BHCVA (see ESI Fig. S9). Observed lengthening of fluorescence lifetime is related with progress of aggregation present in AIE compounds. Furthermore, TA experiments presented shortening of excited state lifetimes. These results were concentration independent which suggests internal processes occurring in the chromophore. Possible explanation could be the steric hindrance of the chromophores in the aggregate that may affect the charge and energy transfers in the confined molecular system that has larger density of excited-states.

In summary, by taking advantage of the direct measurement of two-photon absorption cross section using the Z-scan technique we have provided the first experimental evidence that the aggregation of AIE-active compounds increases their intrinsic σ_2 . Thus, in the context of previous reports we emphasize that the increased two-photon excited brightness of AIE molecules is the result of combining the enhancement of quantum yield of fluorescence with the enhancement of intrinsic TPA. Electronic structure calculations evidenced that the observed increase of two-photon response results predominantly from through-bond enhancement mechanisms. which take place due to formation of aggregates. Aggregation

leads to planarization of the aromatic vinyl bond-anthracene dihedral angle, which enhances the electron delocalization across the molecule. This phenomenon is assisted by the decrease of the detuning factor, which, according to quantum mechanical sum-over-states expressions, leads to the increase of two-photon absorption probability.

We acknowledge the financial support from the Polish Science Centre under DFC-National "Maestro" 2013/10/A/ST4/00114 grant and the Faculty of Chemistry, Wrocław University of Science and Technology. We also gratefully acknowledge the instrumental grant 6221/IA/119/2012 from the Polish Ministry of Science and Higher Education. The calculations were performed at the Wroclaw Center for Networking and Supercomputing.

Conflicts of interest

The authors declare no conflict of interest.

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