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Aggregation-induced emission of [3]cumulenes functionalized with heptagon-containing polyphenylenes

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Lighting on the fluorescence of [3]cumulenes: we report the luminiscence at room temperature by aggregate formation of [3]cumulenes functionalized with propeller-like heptagon-containing polyphenylenes. These endgroups turn on the emission of a [3]cumulene by steric protection and restriction of their intramolecular rotations in the aggregates.

[n]Cumulenes, organic molecules with n double bonds in a contiguous sequence, have attracted increasing interest in recent years as promising model compounds for the understanding of carbyne.[1] In comparison to other related conjugated molecules as polyenes or polyynes, [n]cumulenes are more reactive and therefore less stable. Nevertheless, extraordinary synthetic efforts have been made and thus the structural and electronic properties of [3] to [9]cumulenes have been studied by X-ray crystallography and UV-Vis absorption spectroscopy.[2] However, photoluminescence properties of [n]cumulenes remain almost unexplored.[3] As planar conjugated systems, [n]cumulenes tend to easily aggregate leading to the quenching of their emission. Aggregation-caused quenching (ACQ) is a general effect of conventional π-conjugated chromophores which limits their applications in biological aqueous media or as solids or films. In contrast to ACQ, the alternative phenomenon of aggregation-induced emission (AIE) has received major attention since B. Z. Tang *et. al*. described it in 2001[4] and extensive progress and many applications have been reported.[5] Typical examples of structural motifs present in AIE-active molecules are hexaphenylsilole (HPS) or tetraphenylethene (TPE, Chart 1).[6] As AIE-luminogens, both compounds are non-emissive in solution, as solvation allows the rotation of their phenyl rings which dissipates their excited-state energy by a non-radiative deactivation. In contrast, their emission is activated upon aggregation due to the restriction of the intramolecular motion (RIM) of the phenyl rings resulting in slower non-radiative decay rates and higher fluorescence emission yields.

We envisioned that the introduction of adequate endgroups could turn on the emission of [3]cumulenes at room temperature in polar media as a result of an AIE phenomenon. Hence, herein we report that the steric protection of the [3]cumulene fluorophore by propeller-like heptagon-containing polyphenylenes as endgroups turns on its emission upon aggregation (Chart 1, compound **1**). In addition, we show the two-photon based upconversion of the [3]cumulene **1**-aggregates. This strategy opens up the possibility of using [n]cumulenes as active luminogens upon aggregation.

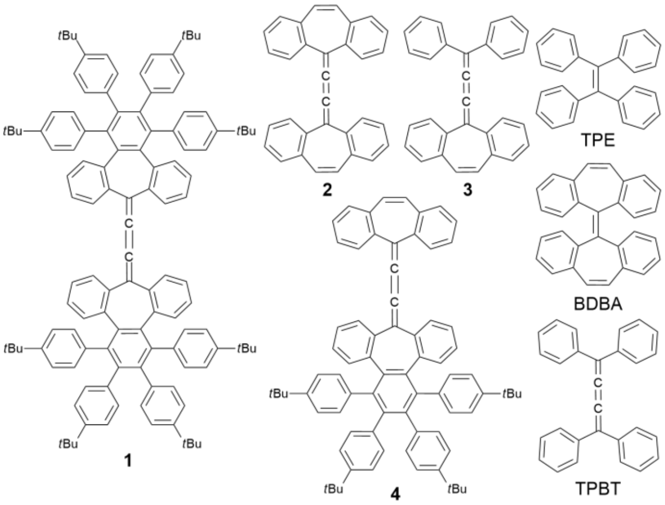

Chart 1 Compounds studied as AIE-emitters: [3]cumulene derivatives **1-4** and tetraphenylbutatriene (TPBT). Related previously reported AIE-luminogens tetraphenylethene (TPE)[6b] and 5,5'-dibenzo[a,d][7]annulenylidene (BDBA)[10].

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Electronic Supplementary Information (ESI) available: General details, synthesis and spectroscopy data. Experimental details on optical measurements. Crystal data and structure refinement of compounds **1**, **3**, **8** and TPBT. CCDC 1817320-1817323. Further details on theoretical calculations and Cartesian coordinates of computed structures. See DOI: 10.1039/x0xx00000x

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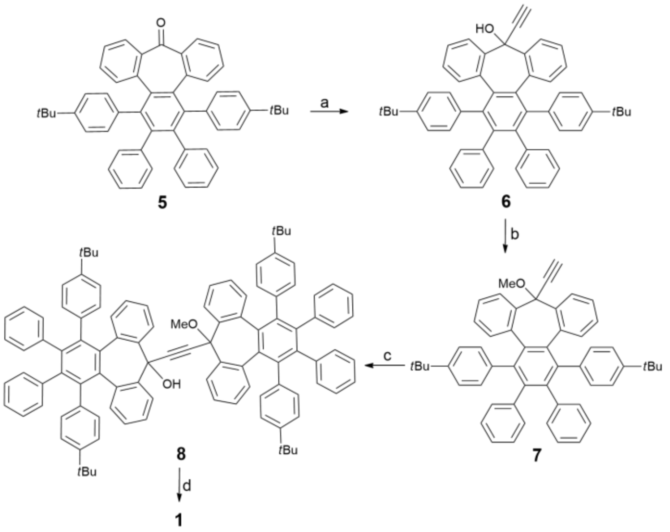
Many structural modifications from the archetypical AIE molecule tetraphenylethene (TPE, Chart 1) have been reported leading to tunable emission and a great variety of technological applications.[7] The replacement of the ethene stator by a longer [3]cumulene moiety leads to tetraphenyl-[3]cumulene (1,1,4,4-tetraphenylbutatriene, TPBT, Chart 1) that is not emissive in solution at room temperature but it is highly emissive when isolated in a solid matrix at low temperature.[3] This observation suggested that the restriction of the intramolecular motion could effectively induce AIE in TPBT, thus opening up the possibility of having [n]cumulenes as fluorophores in solution. Since the photoluminescence properties of TPBT-aggregates in solution have not been reported yet, we firstly synthetized TPBT by following a described procedure[8] (see ESI for details). In agreement with earlier studies in *n*-hexane,[3] TPBT in THF solution was almost non-emissive (ϕ_F = 0.2%). Systematically increasing the percentage of water in THF, a non-solvent of TPBT, failed to improve the efficiency of fluorescence emission and TPBT resulted non-active as aggregated-induced emitter (see ESI, Fig. S25). Likewise, the systematic replacement of the endgroups by dibenzo[a,d][7]annulenes in compounds **2**[9] and **3**, following a strategy similar to that in the AIE-active BDBA molecule (Chart 1),[10] resulted in no detectable enhancement of the fluorescence emission (see ESI, Fig. S20, S22). In these cases no emission was detected from neither the monomers in THF nor the aggregates in water/THF mixtures, suggesting that the restriction of intramolecular vibration (RIV) is not enough to activate the AIE in the case of [3]cumulenes.[11] Most likely, the longer [3]-cumulene fluorophore in **2**, **3** and TPBT in comparison with ethylene in TPE or BDBA requires bulkier endgroups that sterically protect both cumulene faces to avoid strong π-π stacking interactions at solid or aggregated states.



Scheme 1 Synthesis of compound **1**. Reagents and conditions: a) Ethynylmagnesium bromide, THF, –40 °C to rt , 16 h, 79%; b) NaH, DMF, 0 °C, 30 min; then MeI, DMF, rt, 1 h, 99%; c) *n*BuLi, THF, –78 °C, 30 min; then **5**, THF, –78 °C to rt, 16 h, 13%; d) $SnCl_2 \cdot 2H_2O$, HCl, Et_2O, 1 h, rt, 45%.

A good strategy to introduce such bulkier propeller-like polyphenylenes as [3]-cumulene endgroups might be using aryl-substituted tetraphenyl groups or hexaphenylbenzene adducts present in AIE active TPE derivatives.[12] Alternatively, given the versatile synthetic methodology recently developed by our group[13] to prepare heptagon-containing polyphenylenes,[14] we envisioned that the introduction of these bulky endgroups could be a good strategy to turn on the AIE of [3]cumulene. Thus, we obtained compound **1** in 4 steps starting from the described ketone **5**,[13] by a similar synthetic route as previously reported for TPBT based on reaction with BrMg-acetylide, formation of methyl ether **7** followed by a second addition reaction to ketone **5** and final reductive elimination from the methoxyhydroxybutyne derivative **8** with classic $SnCl_2$/HCl conditions, (Scheme 1). Compound **1** was characterized by means of HRMS (MALDI-TOF) and ^{1}H- and ^{13}C-NMR and IR spectroscopies, confirming the presence of the [3]cumulene core.

Single crystals of **1** and **8** were grown by slow evaporation of solutions in hexane/$CHCl_3$ and hexane/CH_2Cl_2, respectively. X-Ray crystallography revealed the propeller shape of both compounds, showing how the saddle curvature caused by the seven-membered ring together with the polyphenylene unit hide both faces of the planar cores (Fig. 1). The disclosure of the curved structure of the endgroups in **1** was also confirmed with the aid of DFT-based calculations (see ESI, Fig. S33). As previously described for compound **2**[9] (Chart 1), due to the presence of flexible cycloheptatriene moiety, **1** can adopt two stable conformations: *syn* (as obtained by X-Ray crystallography, Fig. 1, left) and *anti* with the endgroups on opposite sides of the [3]cumulene bridge. The DFT (B3LYP/6-31G(d,p)) theoretical free energy of the two possible conformers of **1** showed the *anti* conformer as slightly more stable (ΔG=1.2 Kcal/mol) than the *syn* conformer, similarly to what was found for *syn*-**2** and *anti*-**2** conformers,[9b] suggesting that both compounds exchange at room temperature, although only the *syn* isomer was found in the single crystals obtained upon crystallization from hexane (Fig. 1, left).[9b]

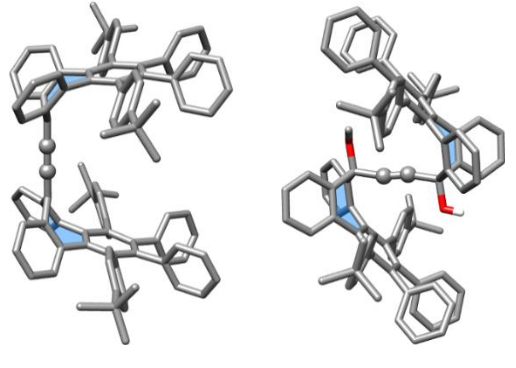


Fig. 1. Lateral view of the X-ray crystal structure of **1** (left) and **8** (right), heptagonal rings showed in light blue. Hydrogen atoms (except that of the OH group) and solvent molecules have been omitted for clarity.

Having synthesized **1**, we firstly evaluated its optical properties in solution. The UV-Vis absorption spectrum of **1** in THF (Fig. 2a) shows a broad absorption band between 325-430 nm with a maximum at 360 nm. The absorption spectra is very well predicted by the DFT calculations (see ESI, Fig. S34). The main contribution to this absorption band is a HOMO-LUMO transition described by an electron density redistribution extending over the central [3]cumulene bridge and both

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dibenzo[a,d][7]annulenes units of the endgroups (see ESI, Fig. S35). The corresponding molar absorptivity was estimated to be 1.6×10^4 M^{-1} cm^{-1}. The photoluminescence emission measurements showed a very weak fluorescence emission band centered at 500 nm with a quantum yield of 0.02. We evaluated the aggregation effect by following the fluorescence emission of **1** at a fixed concentration (ca. 10^{-5} M) in THF/water mixtures with increasing vol % of water, upon excitation at 360 nm. Fig. 2b shows a strong increase in the fluorescence emission with the water content up to 90 vol %. We observe a maximum aggregation enhancement factor of ca. 30 for 70-90 vol % water content with the emission quantum yield reaching a remarkable value of ca. 64% (Fig. 2c). Higher percentage of water led to a decrease in the emission. This effect, previously reported on other AIE-active molecules such as diphenyldibenzofulvenes,[15] has been attributed to the formation of amorphous and weakly luminescent aggregates.

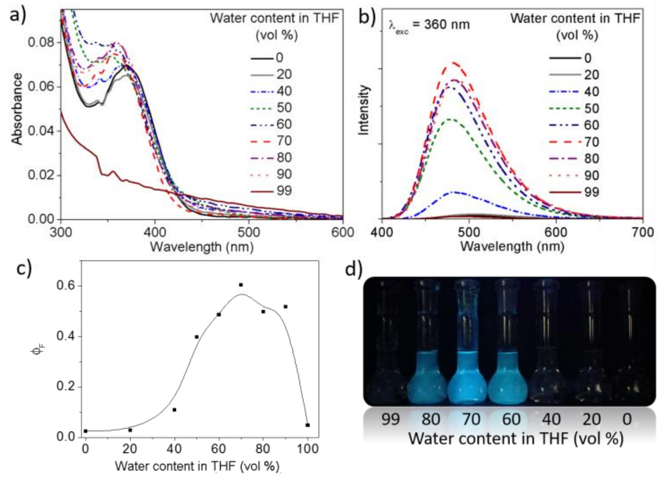

Fig. 2. Photophysical properties of **1** in THF/water mixtures: a) UV-Vis absorbance; b) fluorescence spectra upon excitation at 360 nm; c) fluorescence quantum yield; d) photographs of **1** in THF/water mixtures taken under illumination of a UV lamp.

Transmission electron microscopy (TEM) showed the morphology of **1**-aggregates formed in the mixtures at 70 vol % water content as isolated long aggregates (see ESI, Fig. S36). The size of the **1**-aggregates was estimated by dynamic-light scattering (DLS) (see ESI, Fig. S37). Up to 50 vol % of water content in THF very small aggregates of about 3 nm are observed.[16] Increasing the water ratio resulted in the formation of larger aggregates with a disruptive behaviour between 40-60 vol % water when a second population of bigger aggregates becames relevant. At 60 vol % water two populations of aggregates coexist with 1 μm and about 200 nm size, being the smallest one the dominant population.

The absorption and emission maxima of **1** showed a slight hypsochromic shift of 20 nm with the increasing water ratio, as expected for a nonpolar hydrophobic molecule in the absence of strong π-π stacking interactions, thus excluding the formation of intermolecular excited state dimers in the aggregated state (see ESI, Fig. S17).[17] Similar trend has been observed for other AIE-active molecules.[18]

The excited state lifetime (<τ>) is well described by a monoexponential decay in THF with a time constant of 78 ps. As the water content increases the lifetime becomes multiexponential, and the average lifetime increases by a factor of 30 up to 2.3 ns at 70 vol % water content (see ES, Fig. S18). We evaluated the aggregation effect on the radiative ($k_r = \phi_F/<\tau>$) and non-radiative ($k_{nr} = 1/<\tau> - k_r$) rate constants. The k_{nr} slows down from 12.5×10^9 s^{-1} to 0.2×10^9 s^{-1} while k_r remains practically constant at 0.2×10^9 s^{-1}, thus confirming that the aggregation effect on the emission is due to the RIM slowing down the non-radiative decay rate.

We also studied the optical properties of derivative **4**, incorporating non-symmetrical endgroups at the [3]cumulene core (Chart 1). Aggregation did not activate luminescence of **4** (see ESI, Fig. S23). Those results show that [3]cumulenes behave as efficient AIE-active fluorophore only when both ends of the [3]cumulene core are protected by bulky propeller-like saddle polyphenylenes such as in the case of **1**. To the best of our knowledge, this is the first time that the luminescence of an arylbutatriene is described at room temperature and as a class of AIE-active systems.

AIE molecules may find an enormous set of applications as sensors. In this sense, near-infrared (NIR) excitation is also desirable for biological imaging and AIE together with two-photon induced emission have been reported.[19] Therefore, we explored if **1** is also able to act as a nonlinear fluorophore exhibiting aggregated-induced upconverted fluorescence upon near-infrared excitation.

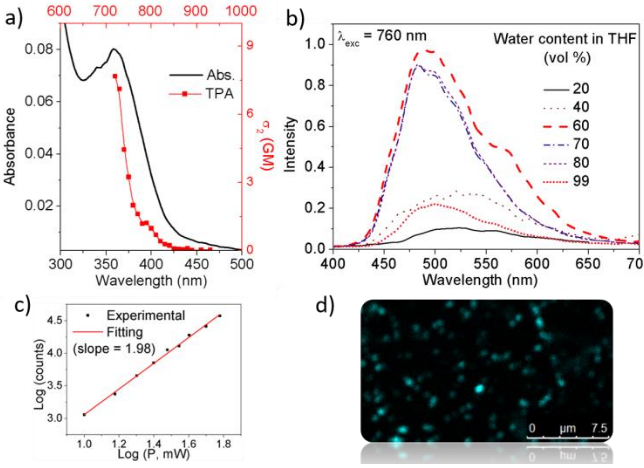

Fig. 3. a) TPA and OPA of **1** in THF/Water mixture with 80 vol % water content; b) two-photon induced emission upon excitation at 760 nm of **1** in THF/water mixtures; c) log-log plot of the two-photon emission *vs* excitation power measured in 80 vol % water content in THF; d) multiphoton fluorescence image of **1**-aggregates formed in THF/water mixture with 80 vo l% water content deposited on a glass slide under irradiation at λ=760 nm (scale bar of 5 μm).

Excitation in the 700-950 nm region with a femtosecond laser with a high excitation power density (1 MW cm^{-2}) causes the simultaneous absorption of two NIR-photons. The TPA maximum appears at ca. 730 nm in good agreement with the linear absorption maxima at 360 nm (Fig. 3a). The two-photon induced emission spectrum is coincident with the one induced by a single photon of 360 nm, reaching a maximum of emission at 500 nm with 70 vol % water content in THF (Fig. 4b). The quadratic dependence of the upconverted emission on the

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excitation power was also confirmed (Fig. 4c). Multiphoton fluorescence images showed the formation of emissive aggregates upon increasing water ratio in the mixture, confirming the source of the fluorescence emission (Fig. 4d).

The TPA cross-section (σ_2) of the aggregates cannot be rigorously determined due to the size dispersion of the aggregates and their unknown concentration. Nevertheless, the estimated effective TPA cross-section per molecule of **1** (9 GM) is not significantly affected by aggregation (see ESI, Fig. S26). Thus, **1** demonstrates two-photon excited fluorescence in the aggregated state making [n]cumulene promising materials for nonlinear optical applications.

To conclude, we report on the development of a new class of AIE molecules based on the [3]cumulene moiety. We present the synthesis and photophysical properties of the first reported example of an arylbutatriene fluorogen. Thus, **1** represents the foundation for the use of [3]cumulenes as fluorophores upon aggregation. We have also proved the TPA-based aggregation-induced upconversion for **1**. Those saddle-shaped polyphenylene endgroups could be considered as a new class of stoppers that might be incorporated to sterically protect other reactive moieties avoiding intermolecular interactions while enhancing solubility. Trends in the series of [n]cumulenes as photoluminiscent compounds upon aggregation are now accessible, as well as electronic properties of their excited electronic states. The [3]cumulene-based AIE-active molecules might find many applications as luminogens and sensors. Moreover, the versatile endgroups might also allow a fine-tuning of photophysical properties by the easy introduction of different functional groups in the aromatic rings. Hence, we might envision the synthesis of derivatives to modulate emission wavelength, nonlinear or even chiroptical responses.

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Conflicts of interest

There are no conflicts to declare.

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