Controlling molecular assembling by photons: reversible light-powered monomer–aggregate interconversion of porphyrins†

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Reversible formation and destruction of H-type aggregates of an anionic porphyrin can be controlled exclusively through light inputs of different energy exploiting the different interactions with the two isomeric forms of a cationic photoresponsive azobenzene-based surfactant.

The possibility of reversibly controlling the formation and destruction of chromogenic assemblies by external inputs represents one ultimate goal in supramolecular chemistry, not only for the fundamental interest in controlling molecular motions at the nanoscale but also in the perspective of future optical devices.[1] Light is a very appealing on/off trigger. Its ready availability and easy manipulation, associated with the rapidity and instantaneous initiation/stopping of the photochemical reactions make the photoregulated systems particularly desirable, offering the additional advantage of not affecting important parameters such as temperature, pH, ionic strength *etc*.

Porphyrins constitute one of the most massively investigated families of molecules by virtue of their excellent spectroscopic, photochemical and electrochemical properties.[2] An intriguing characteristic of these macrocycles is their tendency to form aggregates of different order and structure, which have both scientific and technological importance.[3] Of these, those called J- (edge-to-edge molecular arrangement) or H-type (face-to-face molecular arrangement) are found to have unique electronic and spectroscopic properties due to their high order.[4] On this basis, the achievement of the light-powered aggregation–disaggregation of these chromophoric systems represents an exciting objective to pursue.

As a part of our ongoing project on photocontrolled processes in organized porphyrin-based systems,[5] in this contribution we report a simple supramolecular approach for reversibly controlling the monomer–aggregate interconversion of the anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphyrin (TPPS) in water medium exploiting exclusively photons of different energy which are absorbed by a photoswitching center non-covalently linked to the porphryrin.

The work presented herein has its roots in the elegant studies carried out in the groups of Periasamy first[6] and then Tabak,[7] which pointed out that the cationic surfactant cetyltrimethylammonium chloride (CTAC) encourages the formation of premicellar H-type aggregates of TPPS at neutral pH. These aggregates are mainly stabilized by Coulombic interactions between the two oppositely charged species and the hydrophobic clustering of the alkyl chains of the surfactant. Inspired by these results, we have explored the possibility of controlling the aggregation ⇆ disaggregation process of TPPS through a cationic surfactant whose molecular structure, and consequently its interactions with TPPS, can be reversibly changed by light stimuli of different energy. To this end, we have designed and synthesized the amphiphilic molecule **1** which integrates the photochromic azobenzene moiety in its molecular skeleton. We demonstrate that the *trans* ⇆ *cis* photoisomerization of **1** deeply affects the extent of its interaction with TPPS allowing repeated H-aggregate ⇆ monomer interconversion by means of alternate UV and visible light excitation (Fig. 1).

Compound **1** is water soluble, undergoes reversible *trans* ⇆ *cis* photoisomerization upon UVA-Vis light excitation and, analogously to similar cationic azobenzene-based amphiphiles,[8] forms micelles in aqueous solution at critical micellar concentrations (cmc) of *ca*. 3 mM and 7 mM in the case of the *trans* and *cis* form, respectively (Fig. S1,2†). At neutral pH TPPS is present as tetraanion exhibiting a Soret absorption at 412 nm and a double band fluorescence emission with maxima at 640 and 700 nm, respectively.[6,7] The spectroscopic properties of TPPS are profoundly affected by the addition of **1**-*trans* in a concentration range well below the cmc. As shown in Fig. 2A the fluorescence emission is significantly reduced and red-shifted by *ca*. 22 nm. The excitation spectra show a broadening of the Soret band which is hypsochromically shifted by *ca*. 10 nm whereas the Q-bands are all red shifted (Fig. 2B).[9] Fig. 2C shows that the maximum decrease of the fluorescence quantum yield is reached for the ratio [**1**-*trans*]/[TPPS] ≅ 20.

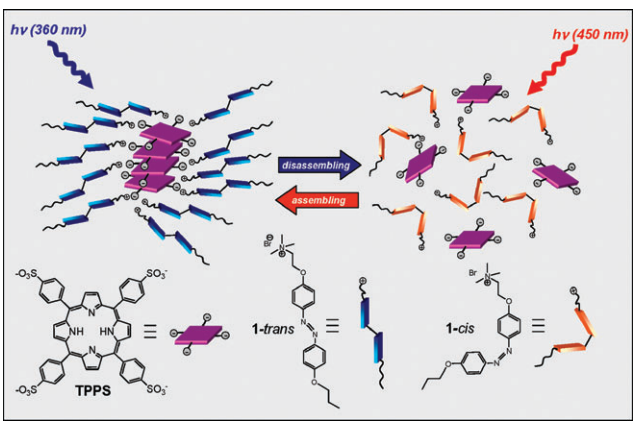

Fig. 1 A schematic view of the light-powered assembling–disassembling of TPPS mediated by **1**.

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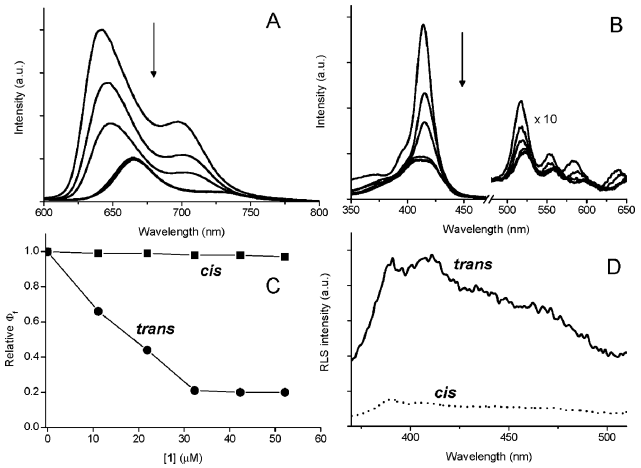

Fig. 2 (A) Fluorescence emission (λ_{exc} = 530 nm) and (B) excitation (λ_{em} = 640 nm) spectra of TPPS (1.5 μM) upon addition of increasing amounts of **1**-*trans* in the range 0–52 μM, in phosphate buffer pH = 7.4, T = 25 °C. (C) Relative fluorescence quantum yield of TPPS observed in the presence of different amounts of **1**-*trans* (●) and **1**-*cis* (■). (D) RLS spectra of the mixture **1**:TPPS at molar ratio 20:1.

This spectroscopic behavior has much in common with that previously observed with the CTAC surfactant and is typical for a face-to-face arrangement of the TPPS units in H-type aggregates.[6,7] However, the low but not negligible fluorescence emission observed in the presence of the azo-surfactant, suggests a deviation from the strict parallel arrangement of the dipole moments of TPPS units.[10] Further evidence for the formation of aggregates is given by resonance light scattering (RLS) measurements, a powerful tool for testing aggregate formation.[11] As shown in Fig. 2D, an intense signal in the correspondence of the Soret absorption band confirms that the aggregate is large enough to scatter the light, providing clear evidence for the involvement of multiple TPPS molecules per aggregate.[12] This hypothesis is in good agreement with the reduced fluorescence quantum yield of the aggregate compared to the monomer because of self-quenching phenomena among TPPS molecules in close proximity.

Experiments performed with the *cis* isomer of **1** show a remarkably different behavior. In fact, the spectroscopic properties of TPPS remain basically unaffected when this compound is added in the same range of concentration of the *trans* species (Fig. 2C) and no significant RLS signal is observed (Fig. 2D). These findings reflect the more polar structure of the *cis* isomer for which the relevance of the hydrophobic contribution to the stabilization of the aggregate is expected to be much smaller than that of the parent *trans*.[13] Short chain surfactants have been in fact demonstrated to be able to induce aggregation only at higher concentrations due to their reduced hydrophobic contributions.[14]

This drastically different behavior between the two isomeric forms of **1** can thus be exploited to reversibly control the destruction and formation of the porphyrin aggregates by the photoisomerization of **1** if its concentration is appropriately chosen. For instance, if the concentration of **1**-*trans* is *ca.* 30 μM, TPPS will be present as H-aggregate (see Fig. 2C). UVA irradiation will induce conversion of the *trans* azo-surfactant into *cis* which, at the above concentration, does not interact significantly with the porphyrins leading to their disassembling into monomers. The validity of our design is illustrated in Fig. 3 where absorption and fluorescence measurements after UVA and Vis excitation are reported together. As displayed in Fig. 3A irradiation with 360 nm light induces *trans* to *cis* isomerization of **1**. Beside, a fluorescence revival of TPPS whose intensity and maxima position are virtually identical to those of the monomeric form, is observed (see, Fig. 3B and 2A, for comparison). Furthermore, the RLS intensity drops dramatically (inset Fig. 3B) confirming the destruction of the H-type aggregates. Irradiation of the system with 450 nm light reverts back the *cis* isomer of **1** into the *trans* form, as confirmed by the almost complete recovery of the UV absorption band (Fig. 3A). Besides, we observe that the fluorescence spectrum decreases to the original value and the RLS signal increases again as consequence of the reformation of the H-type aggregates. The H-aggregate ⇆ monomer interconversion can be switched repeatedly several times by means of alternate UV-Vis light excitation (inset Fig. 3B).

In summary, we have devised a simple strategy for controlling the aggregation–disaggregation of porphyrins, based on two independent components whose interactions can be exclusively controlled by photons of different energy without affecting important parameters such as temperature, pH, ionic strength *etc*. To the best of our knowledge, this represents the first supramolecular approach for reversibly controlling the monomer–aggregate interconversion of porphyrins in an aqueous medium by exploiting exclusively light inputs absorbed by a secondary photoswitching unit non-covalently linked to the porphyrin center.[15] In view of the considerably different spectroscopic and photochemical properties exhibited by the monomeric and aggregate species and their potential in different fields ranging from optical to biological, the strategy illustrated herein represents an appealing starting point for further development of dynamic chemical devices in these research areas.

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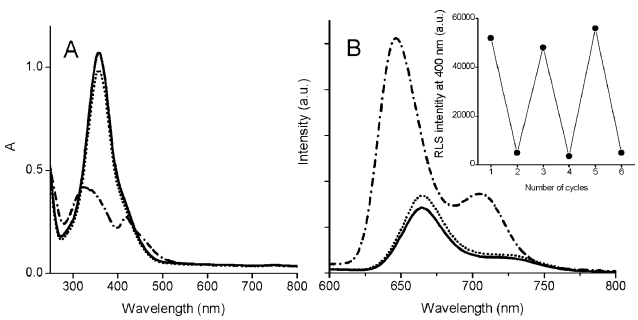

Fig. 3 (A) Absorption spectra of the mixture **1**-*trans*:TPPS (20:1) before (—), after 10 min irradiation with 360 nm light (--) and subsequent 20 min irradiation with 450 nm light (···), in phosphate buffer pH = 7.4, T = 25 °C. (B) Fluorescence emission spectra (λ_{exc} = 530 nm) of the same sample of (A). The inset shows the RLS intensity upon alternate cycles of UV and Vis light irradiation.

Notes and references

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12 An association constant **1**-*trans*/TPPS of *ca.* 1×10^5 M^{-1} was estimated through the fluorescence spectral changes.

13 We cannot rule out that π–π stacking interaction between the aromatic rings of the **1**-*trans* can probably play a key role in the stabilization of the H-aggregates. Such type of interactions are expected to be disfavored in the **1**-*cis* due to its non-flat structure, accounting for the weak affinity of this isomer for TPPS.

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