Synthesis and photophysical characterization of a subphthalocyanine fused dimer–C_{60} dyad†

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Photophysical studies of a newly synthesized fused subphthalocyanine dimer–C_{60} 1 revealed a complex cascade of energy transfer events to succeed the initial SubPc dimer photoexcitation.

Subphthalocyanines (SubPcs)[1]—phthalocyanine analogues—are intriguing compounds made of three diiminoisoindoline units *N*-fused around a boron atom. Their 14 π-electron aromatic core associated with their curved structures renders them appealing building blocks for the construction of multicomponent photo- or electroactive assemblies.[2] Recently, the development of an improved synthetic methodology for SubPc preparation[3] allowed the efficient synthesis of fused subphthalocyanine dimers[4] (**2** in Fig. 1) and trimers, and the separation of their *syn* and *anti* topoisomers (**2a** and **2b**, respectively).[5] Such nonplanar conjugated and aromatic systems are fascinating structures that have been arousing great interest both theoretically[6] and experimentally.[7] For example, SubPc dimers **2a** and **2b** were found to present very different features from those of their corresponding SubPc monomers—both in terms of optical and magnetic properties. To enhance the understanding of the nature of this new π-extended surface, we have studied their photophysical properties and their ability to promote energy or charge transfer processes within a newly synthesised covalent SubPc dimer–C_{60} complex, **1**.

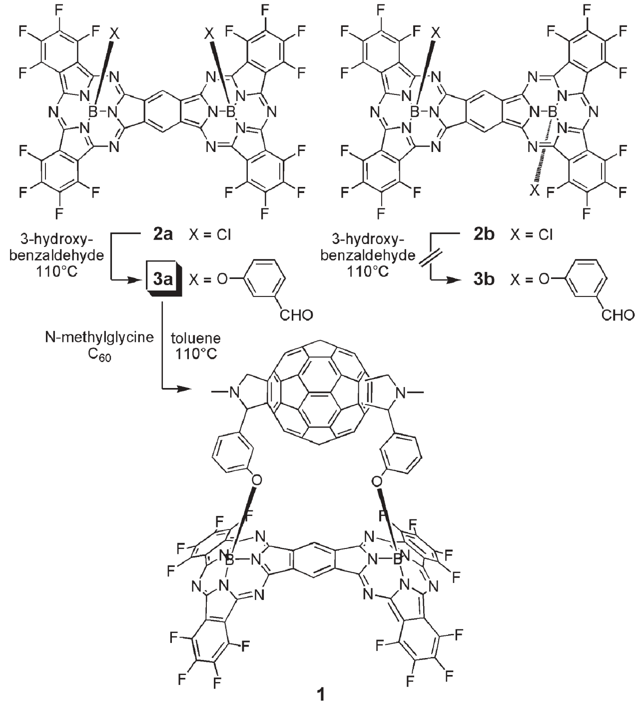

Fig. 1 Synthesis of SubPc dimer–C_{60} **1**.

SubPc dimers **2** were prepared as a mixture of topoisomers *syn* **2a** and *anti* **2b** in 18% yield by statistical condensation of 1,2,4,5-tetracyanobenzene with an excess of tetrafluorophthalonitrile (1–10 M) in the presence of BCl_3 in *p*-xylene at 140 °C for 2–3 h. **2a** and **2b** were separated by column chromatography on silica gel; the *syn* : *anti* ratio being 1 in all cases. Changing the tetracyanobenzene : tetrafluorophthalonitrile ratio from 1 : 1 to 1 : 20 did not improve the overall yield of SubPc dimer formation.

Following a successful two-step procedure developed in the case of monomeric subphthalocyanines,[2a–c] C_{60} was grafted to the SubPc dimers. Thus, the *syn* dialdehyde precursor **3a** was prepared by axial chlorine substitution in 40% yield by reacting SubPc dimer **2a** with 3-hydroxybenzaldehyde in toluene at reflux for 20 h.[3] Surprisingly, the *anti* isomer **2b** gave rise to decomposition products in the same reaction conditions instead of yielding the corresponding dialdehyde **3b**. No rational explanation for this fact has been found so far. The *syn* dialdehyde **3a** was then reacted with *N*-methylglycine and C_{60}, to yield the C_{60} bisadduct[8] SubPc dimer–C_{60} ensemble **1** in 14% yield. **1** was unambiguously characterized by ^{1}H NMR spectroscopy, MALDI TOF mass spectrometry, and elemental analysis. The ^{1}H NMR spectrum of **1** showed an impressive number of broad signals as a consequence of both the presence of a mixture of up to 20 stereoisomers[9] and the dynamic processes occurring within the dyad, *i.e.* slow motion on the NMR time scale of the C_{60} moiety with respect to the SubPc dimer—see supplementary information.†

The extended π-electronic structure of the SubPc dimer core impacts ground and excited state features relative to the monomeric dodecafluorinated SubPc.[2b] In the ground state, drastic red-shifts (573 to 692 nm) parallel those seen in the excited state fluorescence (585 to 708 nm). Other physico-chemical features that reveal appreciable changes are ground state extinction ($\varepsilon_{692\text{nm}}$ = 79 500 M^{-1} cm^{-1}), fluorescence quantum yield (Φ = 0.24 ± 0.01) and fluorescence lifetime (τ = 2.5 ± 0.1 ns—see Fig. S1†).

Double linking C_{60} to **2a** leads, in the ground state, to minute perturbations of the π-electronic structure of the SubPc dimer core. When photoexciting **1**, the fluorescence quantum yields, however, decrease strongly. In toluene, THF and benzonitrile quantum yields are as low as 0.02 ± 0.01—see Fig. 2. Despite the

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† Electronic supplementary information (ESI) available: experimental procedures, NMR, IR, UV, and MS data for **3a** and **1**. Time resolved fluorescence decay and time–absorption profiles of singlet excited state of **2a** and **1**. See http://www.rsc.org/suppdata/cc/b5/b502041g/
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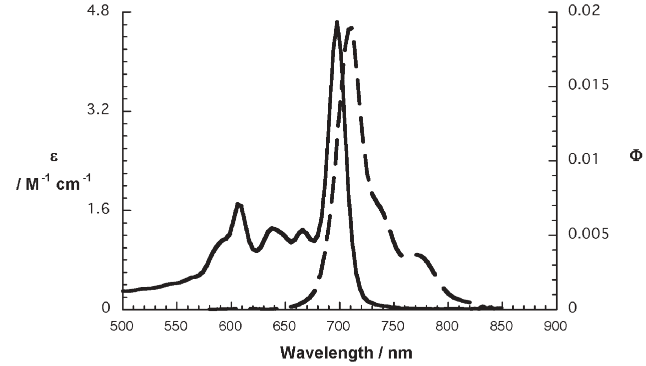

Fig. 2 Absorption and emission of **1** in toluene—exciting at 550 nm.

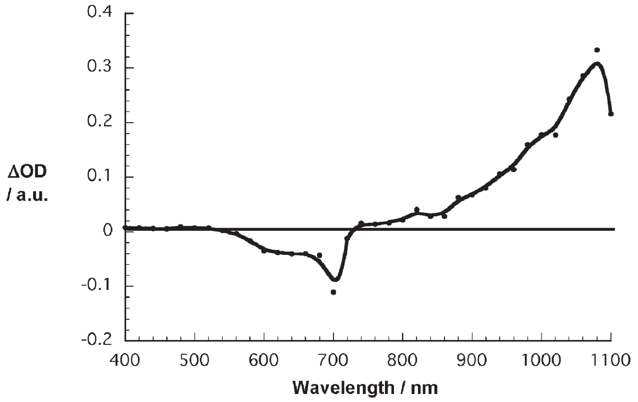

Fig. 3 Differential absorption spectrum (visible and near-IR) obtained upon nanosecond flash photolysis (532 nm) of $\sim 5.0 \times 10^{-6}$ M solutions of **1** in nitrogen saturated toluene with a time delay of 50 ns.

quenching, the fluorescence spectra of **1** and **2a** are strict superimpositions, that is, no quenching products can be assigned based on these experiments. The C_{60} reference fluoresces in the same spectral region with quantum yields of *ca.* 10^{-4}.

Fluorescence decay measurements shed light onto the SubPc dimer deactivation and also onto the photoproducts. Fig. S1 illustrates this for toluene.† The fluorescence–time profiles for **1** are best fitted—with χ^2 values of at least 1—by bi-exponential expressions, while **2a** shows best fits with a mono-exponential expression. In all solvents, a short-lived (*i.e.*, 0.27 ± 0.02 ns) and a long-lived (*i.e.*, 1.2 ± 0.05 ns) component was found. The short lifetime contribution reflects the actual intramolecular deactivation of the SubPc singlet excited state, while the longer-lived contribution resembles that of the C_{60} reference. This observation leads to the postulation that a transduction of singlet excited state energy between nearly isoenergetic states, that is, from SubPc (1.77 eV) to C_{60} (1.76 eV) occurs. Once the singlet excited state energy is funneled to the C_{60} core, intersystem crossing populates the triplet manifold.

Femtosecond laser pulses were employed to visualize the different products. Typical differential absorption, as recorded with several time delays—0 to 4 ps—following photoexcitation of **2a**, are shown in Fig. S2.† A particular strong transient bleach is seen in the Q-band region. The underlying singlet excited state intersystem crosses slowly to the triplet manifold—see Fig. S2.[10] Photoexciting **1** led at early times—10 ps—to the same absorption changes. This confirms the formation of the SubPc dimer singlet excited state. The SubPc dimer singlet–singlet features decay, however, not *via* intersystem crossing, as Fig. S3 indicates a much faster reaction takes place, which lies within the first 250 ps.† Interestingly, simultaneous to the rapid SubPc dimer singlet–singlet decay, the fullerene singlet–singlet features grow-in above 800 nm.

While in the C_{60} reference intersystem crossing (5.0×10^8 s^{-1}) dominates the deactivation of the singlet excited state, this transition decays in **1** with slightly faster kinetics ($\sim 8.5 \times 10^8$ s^{-1}). Instead of forming the C_{60} triplet, attributes of the SubPc dimer triplet excited state were recorded (Fig. 3). Similar kinetics at the 700 nm minimum—Fig. S2—allowed us to follow the SubPc dimer triplet generation. From this we conclude that the rate-determining step is the C_{60} intersystem crossing.

Complementary nanosecond experiments further corroborated the femtosecond experiments. First, we probed **2a** in toluene, THF and benzonitrile and obtained differential absorption changes that are identical to those depicted in Fig. 3. We determined for this oxygen-sensitive triplet intermediate (*i.e.*, $k_{\text{oxygen}} \sim 10^9$ M^{-1} s^{-1}) lifetimes of around 90 ± 10 μs. Then **1** was studied—a spectrum is shown in Fig. 3—and compared to **2a**. The differential absorption changes are absolutely identical. They indicate that the only detectable photoproduct is that of the SubPc dimer triplet excited state with a 1080 nm peak, a long lifetime (107 μs) and a high triplet quantum yield (95% of that seen for **2a**).

In summary, a cascade of energy transfer events succeeds the initial SubPc dimer photoexcitation. The intriguing molecular geometry of **1** opens the possibility to explore the properties of other photo and electroactive SubPc dimer-based ensembles.

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9 The bisaddition to C_{60} may result in up to 8 isomers if considering only the addition to the [6,6] double bonds. Elementary molecular modeling indicates that *trans*-**1**, *trans*-**2** and *trans*-**3** are the only ones attainable. Regiosisomers *trans*-**2** and *trans*-**3** are racemic mixtures of two enantiomers. Finally, these 5 stereoisomers become 20 as a consequence of the chirality of the two pyrrolidine rings.

10 Apparently the deactivation is slower than our experimental time window of 1500 ps, but it is safe to assume that the fluorescence lifetime of 2.5 ± 0.1 ns is a good estimate for the singlet lifetime.