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PAPER

Subphthalocyanine-polymethine cyanine conjugate: an all organic panchromatic light harvester that reveals charge transfer†

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The synthesis and photophysical characterization of a subphthalocyanine-polymethine cyanine panchromatic light harvester is described. The new conjugate shows the extraordinary absorption features of both constituents and reveals electron transfer that evolves from both constituents.

Introduction

Solar energy represents an unlimited and renewable energy power supply. As a matter of fact, in recent years a great deal of research effort has been invested towards improving artificial systems capable to collect the photonic energy throughout the entire solar spectrum.[1] In this respect, even if organic sensitizers are known to commonly absorb only in the UV and visible regions of the solar spectrum, they have attracted extensive attention because of their synthetic versatility and electronic tunability.[2] In an ideal design, not only the electrochemical and photophysical properties of organic sensitizers should be considered, but also their absorption features. Importantly, the latter determines the upper limit of the photoconversion performances. Notwithstanding, it is important to note, that nowadays molecular systems displaying absorption features in the near-infrared part of the solar radiation, still remain quite scarce and limited.

Motivated by the aforementioned, we were successful in ascertaining the suitability of cationic and anionic heptamethine cyanines as near-infrared light harvester in electron donor–acceptor conjugates.[3] Our photophysical studies revealed that even higher singlet excited states of these cyanines are powerful promoters for charge separation when they are, for example, covalently linked to an electron accepting fullerene. Despite this unique reactivity, the low-to-moderate extinction coefficients of

fullerenes prompted us to explore subphthalocyanines (SubPcs) as electron acceptor in a new generation of heptamethine cyanine conjugates. SubPcs[4]—non-planar aromatic compounds related to phthalocyanines[5]—are known to absorb in the visible region with high extinction coefficients. This renders them particularly appealing for the construction of panchromatic molecular hybrids. To this end, a series of multicomponent systems, in which SubPcs are linked to either electron acceptors or electron donors, are known to date.[6]

Herein, we report the synthesis and photophysical characterization of a cyanine derivative, which converge complementarily the extraordinary near infrared and visible light absorption features of heptamethine cyanines and dodecafluoro boron-SubPc, respectively, in a new panchromatic electron donor–acceptor conjugate (**1**)—see Fig. 1.

Results and discussion

Synthesis

The synthesis of **1** was carried out by axial substitution on chloro-SubPc **2**[7] using polymethine cyanine **4** as nucleophile
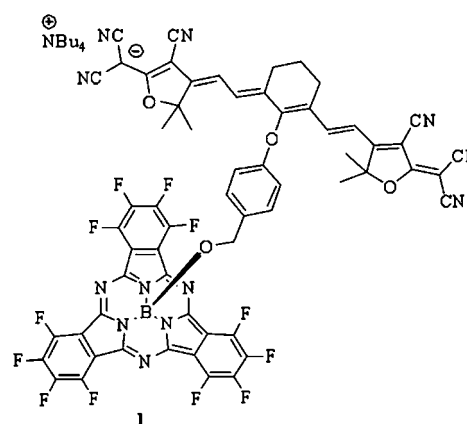
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Fig. 1 Structure of subphthalocyanine-polymethine cyanine (SubPc-cyanine⁻) **1**.

(Scheme 1). We employed a recently developed methodology that makes use of a highly activated triflate intermediate which is generated *in situ* by reaction between chloro-SubPc **2** and silver triflate.[8] Such activation was found to be necessary, since the direct substitution reaction between **4** and **2** ultimately resulted in SubPc decomposition due to the higher temperatures required. On the other hand, **4** was prepared by the substitution of the *meso*-chlorine atom of **3**[3a] by 4-hydroxybenzyl alcohol in DMF. **1** was obtained in 25% yield and characterized by ^{1}H-NMR, MALDI-TOF and HR-MS and UV-vis. Fig. 2 shows the ^{1}H NMR spectrum of **1**. It is interesting to remark that the signal of the benzylic protons is affected by the SubPc ring current causing an upfield shift from 4.39 (**4**) to 2.49 (**1**) ppm (see Inset in Fig. 2). These kind of shifts are very typical in axially substituted SubPcs. Additional experimental details regarding the characterization of compounds **1** and **4** are given in the Supporting Information.

Photophysics

SubPc-cyanine[−] conjugate **1** is a black solid, which, importantly, shows a panchromatic absorption over the entire range between 350 and 1000 nm—see Fig. 3 and S8 (ESI†). Moreover, two stronger absorption maxima evolve at 571 and 903 nm, which correspond to the SubPc and the polymethine cyanine constituent, respectively.

Turning to the electronic communication between the SubPc and polymethine moieties, the first insights into excited state interactions came from fluorescence experiments by means of probing either the SuPc in the visible or the cyanine emission in the near infrared in benzonitrile—see Fig. S8 (ESI†). Firstly, we focused on the visible fluorescence of SubPc upon excitation at 560 nm. Here, the SubPc reference **2** gives rise to fluorescence features that include a fluorescence maximum at 583 nm, a fluorescence quantum yield of 0.58, and a fluorescence lifetime of 3.2 ns. In sharp contrast, in the SubPc-cyanine[−] conjugate **1** the fluorescence quantum yield is reduced to 8×10^{-3} and a lifetime below the detection range of our apparatus (*i.e.*, 0.1 ns). Not impacted is, however, the fluorescence maximum. Secondly,
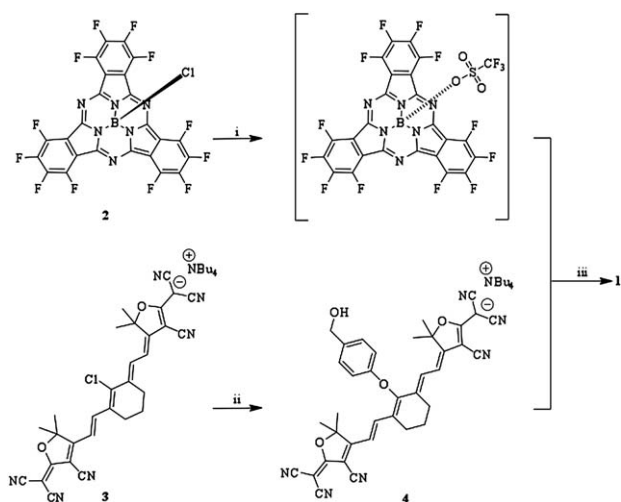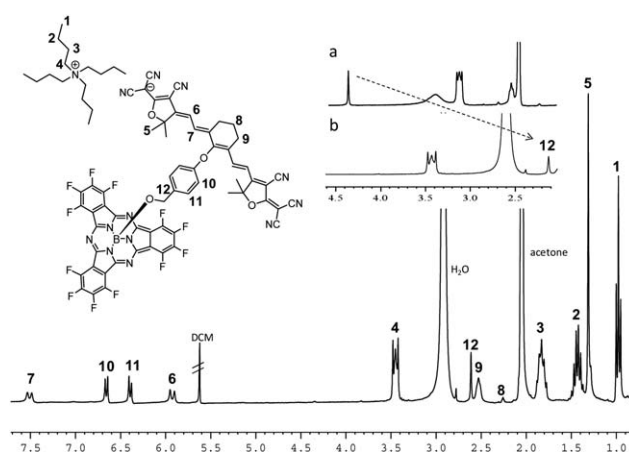
Fig. 2 ^{1}H-NMR (acetone-d_6, 300 MHz) of **1** with proton assignment. Inset: portion of the ^{1}H-NMR spectra of **4** (a) and **1** (b) showing the upfield shift experienced by the methylene proton signal.

800 nm excitation was employed to probe the cyanine fluorescence in the near infrared. A fluorescence maximum at 925 nm and a fluorescence quantum yield of 0.21 are characteristics of the cyanine reference **4**. In the SubPc-cyanine[−] conjugate **1** quenching reduces the fluorescence quantum yield to 0.07. In terms of excited state deactivation mechanism, we inspected the near infrared emission of the cyanine upon SubPc excitation at 560 nm, where the cyanine absorption contributes less than 3% to the overall absorption in SubPc-cyanine[−] conjugate **1**. Here, the insignificant cyanine fluorescence suggests an intramolecular deactivation *via* electron transfer rather than *via* energy transfer.

Next, we turned to transient absorption measurements to confirm the excited state deactivation and to identify the corresponding photoproducts. Like in the fluorescence experiments, selecting different excitation wavelengths helps to monitor processes of the SubPc-cyanine[−] conjugate **1** that exclusively evolve from SubPc or cyanine. In particular, 560 nm was chosen to excite SubPc in the reference **2** and in SubPc-cyanine[−] conjugate **1**. With the conclusion of the excitation of the SubPc reference the following singlet excited state features evolve— maxima at 430, 615, 755, 825, 910, 1070 nm and minima at 515, 560, 630 nm—Fig. S9 (ESI†). The latter transforms with 1.6 ± 0.1 ns into the corresponding triplet excited state *via* intersystem crossing—Scheme S1 (ESI†). Maxima at 460 and 645 nm as well as a minimum at 560 nm emerge as fingerprints of the SubPc
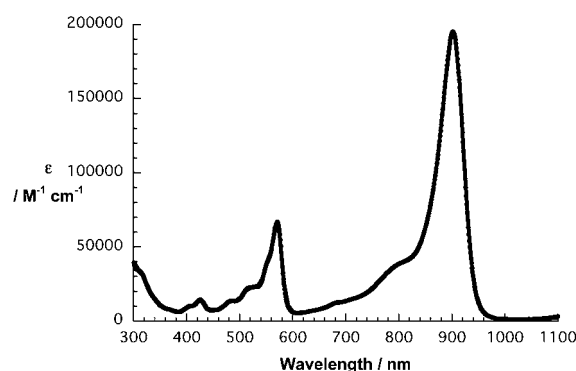
Scheme 1 Synthetic route to **1**. Reagents and conditions: (i) silver trifluoromethanesulfonate, chloroform; (ii) 4-hydroxybenzyl alcohol, NaH (60%), HCl, DMF; (iii) DIPEA, chloroform, 45 °C

Fig. 3 Absorption spectrum of SubPc-cyanine[−] conjugate **1** in benzonitrile.

triplet excited state. The triplet is long-lived as we have confirmed in recent experiments.[6a]

The SubPc-cyanine⁻ conjugate **1** shows initially the same SubPc singlet excited state features when exciting at 560 nm, despite the cyanine presence—see Fig. 4. Maxima at 440, 605, 755, 820, 920, and 1070 nm are complemented by minima at 510, 560 and 630 nm. Importantly however, the cyanine exerts a strong impact on the excited state dynamics. Instead of the slow intersystem crossing (*i.e.*, 1.6 ± 0.1 ns) observed for SubPc reference **2**, all of the aforementioned features decay with 5.7 ± 0.5 ps—a finding that agrees with the efficient fluorescence quenching. With exactly the same time constant new transitions develop. In fact, two sets of transitions are registered. On one hand, in the visible range maxima at 460, 505, 520, and 605 go hand in hand with minima at 495 and 560 nm. On the other hand, maxima at 622, 660, and 730 nm are accompanied by a strong minimum in the near infrared at 890 nm.

Previous investigations have shown that electrochemical and pulse radiolytical reduction of SubPc reveal the same fingerprint than what is seen in the visible.[3a] Likewise, oxidation of cyanine by electrochemistry or pulse radiolysis matches the near infrared transitions.[3a] In other words, the SubPc singlet excited state (2.2 eV) is the inception to a rapid and strongly exothermic charge transfer process to afford the SubPc•⁻–cyanine charge separated state—see Scheme 2. The latter, for which we have determined an energy of 1.1 eV, is short lived and decays with 205 ± 10 ps. Despite its low energy, charge recombination populates the triplet excited state of cyanine—*vide infra*.

Next, we focused on either 387 or 778 nm excitation of the cyanine in both the SubPc-cyanine⁻ conjugate **1** and the reference **4**. 387 nm excitation of the cyanine reference **4** leads to instantaneously formed higher singlet excited state features maxima at 490, 600, and 680 nm, minima at 565, 630, and 735, and broad bleach between 820 and 955 nm – not shown. With a lifetime of 4.4 ± 0.5 ps these features transform rapidly into those of the lowest singlet excited state with distinct maxima at 520, 585, 625, and 1240 nm plus distinct minima at 730 and 920 nm.
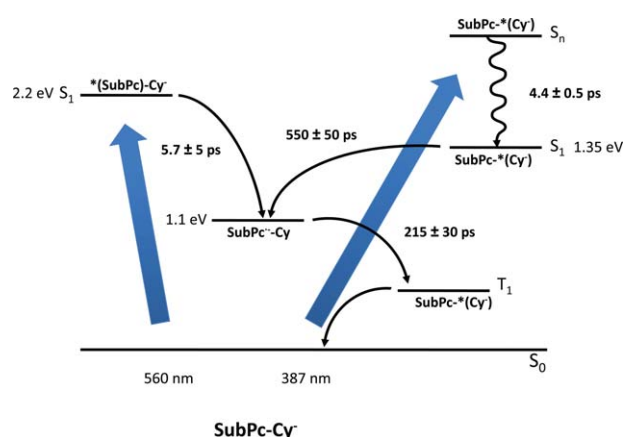
Next, the slow decay of the singlet excited state follows within approximately 2.0 ± 0.5 ns to form correspondingly the triplet excited state—Scheme S1 (ESI†). Population of the higher lying singlet excited states was successfully bypassed by means of excitation at 778 nm. This leads to the rapid (>0.5 ps) and direct formation of the lowest singlet excited state. The lifetime of the correspondingly formed singlet excited state as determined from a multi wavelength analysis is 1.9 ± 0.5 ns.

In the SubPc-cyanine⁻ conjugate **1**, when exciting at 387 nm, the higher singlet excited state internally convert with the same dynamics that the cyanine reference **4** shows, that is, 4.4 ± 0.5 ps, into the lowest singlet excited state (1.35 eV)—see Fig. S10 (ESI†). Commencing with the completion of this process starts the decay of the 490, 600, 680 nm maxima as well as the 565, 630, 735, 905 nm minima. The dynamics of these new transients (*i.e.*, 215 ± 30 ps) are, however, notably faster than the intersystem crossing (*i.e.*, 2.0 ± 0.5 ns) observed for the cyanine reference **4** and, interestingly, match those of the charge recombination seen upon excitation of the SubPc moiety at 560 nm—*vide supra*. Nevertheless, despite these fast dynamics the spectral features of the cyanine triplet excited state emerge simultaneously. A likely rationale must infer a slow charge
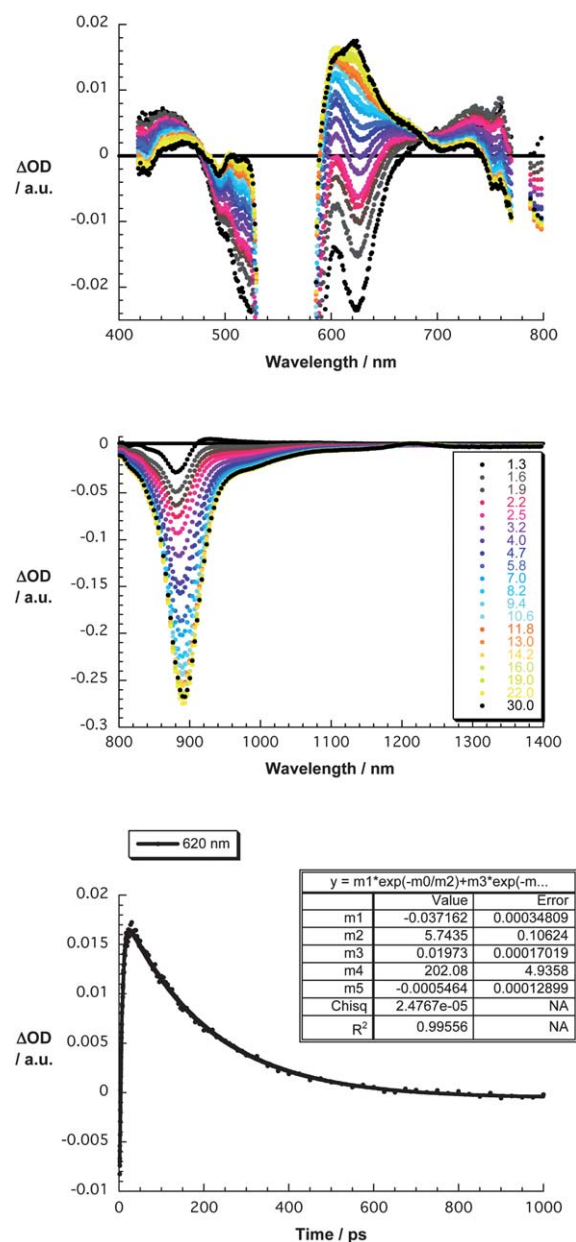
Fig. 4 Upper part – differential absorption spectra (visible) obtained upon femtosecond flash photolysis (560 nm, 150 nJ) of SubPc-cyanine⁻ conjugate **1** in benzonitrile with several time delays between 0 and 30 ps at room temperature – see figure legend of central part for time evolution. Central part – differential absorption spectra (near-infrared) obtained upon femtosecond flash photolysis (560 nm, 150 nJ) of SubPc-cyanine⁻ in benzonitrile with several time delays between 0 and 30 ps at room temperature – see figure legend for time evolution. Lower part – time-absorption profile of the spectra at 620 nm, monitoring the charge separation and charge recombination dynamics.

separation (*i.e.*, 550 ± 50 ps), which has been derived from the fluorescence experiments, followed by a faster charge recombination (*i.e.*, 215 ± 30 ps) to populate the lowest triplet excited state, that is, the cyanine centered one—Scheme 2. In other words, the charge separated state originated from the lowest excited state of the cyanine decays faster than being formed, which renders its detection impossible.

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Scheme 2 Energy diagram of the SubPc-cyanine⁻ conjugate **1**. The dynamics when exciting at 387 and 560 nm are represented.

Conclusions

We have described the synthesis of a boron subphthalocyanine/polymethine cyanine conjugate. In the new conjugate, the complementary characteristics of the heptamethine cyanines, that is, near-infrared absorption and electron donation, with those of dodecafluoro SubPc, that is, visible absorption and electron acceptance, are combined. Although in the ground state no appreciable interactions are seen between the different constituents, in the excited state an intramolecular electron transfer prevails. Importantly, the different singlet excited state energies of 2.2 eV (SubPc) and 1.35 eV (cyanine) relative to the charge separated state energy of 1.1 eV evoke very different charge separation dynamics—5.7 ± 0.5 ps *versus* 550 ± 50 ps, while the charge recombination is not effected at all with 215 ± 30 ps.

Experimental section

General Procedures

LSI-MS and HRMS spectra were determined on a VG AutoSpec apparatus, ESI-MS spectra were obtained from an Applied Biosystems QSTAR equipment, and MALDI-TOF-MS spectra were obtained from a BRUKER ULTRAFLEX III instrument equipped with a nitrogen laser operating at 337 nm. NMR spectra were recorded with a BRUKER AC-300 (300 MHz) instrument. The temperature was actively controlled at 298 K. Chemical shifts are measured in ppm relative to tetramethylsilane (TMS). Carbon chemical shifts are measured downfield from TMS using the resonance of the deuterated solvent as the internal standard. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F254 (E. Merck).

UV/Vis spectra were recorded with a Hewlett-Packard 8453 and Varian Cary 5000 UV-VIS-NIR instruments. The fluorescence experiments were carried out using a Horiba Jobin Yvon Fluoromax 3P and Horiba Jobin Yvon Fluorolog-3 spectrometer. The quantum yields were determined using cresyl violet in methanol (QY = 0.54) and IR-140 in ethanol (QY = 0.167)[9] as standards for the SubPc and cyanine respectively. The fluorescence-lifetime measurements were performed by time correlated single photon counting (TCSPC) by using a FluoroLog-3 spectrometer.

Femtosecond transient absorption studies were performed with 775 and 387 nm laser pulses in benzonitrile (1 kHz, 150 fs pulse width, 200 nJ) from an amplified Ti/sapphire laser system (Model CPA 2101, Clark-MXR Inc.—output 775 nm).

Chemicals were purchased from commercial suppliers and used without further purification. Solid, hygroscopic reagents were dried in a vacuum oven before use. Reaction solvents were thoroughly dried before use by means of standard methods. The synthesis and characterization of the starting anionic polymethine cyanine[3a] **3** and dodecafluorosubphthalocyanine[7] **2** have been previously reported.

Cyanine 4

4-Hydroxybenzyl alcohol (33.6 mg, 0.27 mmol, 1.2 equiv.) was dissolved in dry DMF (8 ml) under argon atmosphere, then NaH 60% (10.8 mg, 0.27 mmol, 1.2 equiv.) was added. After 30 min of stirring at room temperature, **3** (175 mg, 0.23 mmol, 1 equiv.) dissolved in DMF (8 ml), was added dropwise to this solution. The solution was stirred for 6 h at RT under argon atmosphere, and then poured into ice and hydrochloric acid (0.4 ml). The resulting green solid was filtered off, redissolved in dicholoromethane, and washed with water and Na_2CO_3. The organic layer was dried with $MgSO_4$, and precipitated in pentane, to afford **4** as a green solid (160 mg, 84%). ¹H-RMN δ_H(DMSO-d_6; 300 MHz) 7.67 (2H, d, $J = 14$ Hz), 7.22 (2H, d, $J = 8$ Hz), 6.91 (2H, d, $J = 8$ Hz), 5.96 (2H, d, $J = 14$ Hz), 4.39 (2H, s), 3.18–3.13 (8H, m), 2.59–2.56 (4H, m), 1.88–1.83 (2H, m), 1.59–1.54 (8H, m), 1.38 (12H, s), 1.34–1.24 (8H, m), 0.93 (12H, t, $J = 7$ Hz). ¹³C-NMR δ_C(DMSO-d_6; 125 MHz) 176.1, 166.5, 160.9, 158.0, 137.0, 136.0, 128.0, 123.2, 115.4, 114.5, 114.3, 113.9, 105.9, 95.0, 82.5, 62.3, 57.5, 57.5, 57.5, 44.5, 26.1, 23.8, 23.0, 20.7, 19.1, 13.4. MS (ESI -): m/z calculated for $C_{37}H_{27}N_6O_4$: 621.22558 [M]: found 621.22291.

Subphthalocyanine-polymethine cyanine 1

In a 25 mL round-bottomed flask equipped with a magnetic stirrer, **2** (70 mg, 0.11 mmol, 1 equiv.) and silver trifluoromethanesulfonate (36 mg, 0.14 mmol, 1.3 equiv.) were placed. Freshly distilled chloroform (2 mL) was added and the mixture was stirred for 24 h under argon atmosphere until the starting subphthalocyanine was consumed. After that time, compound **4** (20 mg, 0.023 mmol, 0.2 equiv.) and N,N-diisopropylethylamine (0.23 mmol, 0.2 equiv.) were added. The mixture was stirred at 45 °C until the reaction was completed (the reaction was monitored by TLC). The solvent was removed by evaporation under reduced pressure and the product was purified by chromatography on silica gel using DCM/ethyl acetate (3 : 1) as eluent. Recrystallization from DCM/hexane afforded compound **1** as a black solid. Yield: 25%. ¹H-NMR δ_H(300 MHz; (CD₃)₂CO) 7.37 (2H, d, $J = 14.7$ Hz), 6.53 (2H, d, $J = 8.7$ Hz), 6.27 (2H, d, $J = 14.7$ Hz), 5.79 (2H, d, $J = 14.7$ Hz), 3.32 (8H, m), 2.49 (2H, s), 2.45–2.35 (4H, m), 2.16–2.10 (2H, m), 1.80–1.61 (8H, m), 1.39–1.23 (8H, m), 1.19 (12H, s), 0.85 (12H, t, $J = 7.2$). MS (MALDI, DCTB): $m/z = 1473$ (M⁻, 5%), 1231.2 ([M-NBu₄⁺]⁻, 100%), 621.0 ([Cy]⁻). HRLSI-MS ($C_{77}H_{64}BF_{12}N_{13}O_4$) [M]⁻ Calculated: 1473.5106; Found: 1473.5082. UV-vis: λ_{max}(CHCl₃)/nm 892, 789sh, 569, 554sh, 524sh, 430, 313, 282.

Acknowledgements

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