Excited State Interactions in Calix[4]arene–Perylene Bisimide Dye Conjugates: Global and Target Analysis of Supramolecular Building Blocks

Catharina Hippius,[†] Ivo H. M. van Stokkum,[‡] E. Zangrando,[§] René M. Williams,^{*,||} and Frank Würthner^{*,†}

Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Am Hubland, D-97074 Würzburg, Germany, Molecular Photonics Group, van't Hoff Institute for Molecular Sciences (HIMS), Universiteit van Amsterdam, Nieuwe Achtergracht 129, WS 1018 Amsterdam, The Netherlands, Department of Physics and Astronomy, Vrije Universiteit, de Boelelaan 1081, 1081 HV Amsterdam, The Netherlands, and University of Trieste, Dipartimento di Scienze Chimiche, Via Licio Giorgieri 1, 34127 Trieste, Italy

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The photophysical properties of two supramolecular building blocks **oc** and **oc2** consisting of a perylene bisimide chromophore substituted with either one or two calix[4]arene units in the *N*-imide position as well as those of the reference compound **oref** without calix[4]arene substituents were investigated. A complete picture of the processes taking place after photoexcitation in toluene, CH₂Cl₂, and benzonitrile was obtained by means of UV/vis absorption, steady state and time-resolved emission, and femtosecond transient absorption spectroscopy. It has been found that the fluorescence emission of compounds **oc** ($\Phi_{\rm fl} = 0.03$ in CH₂Cl₂) and **oc2** ($\Phi_{\rm fl} < 0.01$ in CH₂Cl₂) is almost completely quenched compared with the highly emissive reference compound **oref** ($\Phi_{\rm fl} = 0.99$ in CH₂Cl₂) because of fast electron-transfer processes from the calix[4]arene moieties to the perylene bisimide chromophore. This predominantly takes place with rate constants of $k_{\rm CS} = 3 \times 10^{10} \text{ s}^{-1}$ ($\tau_{\rm CS} = 32 \text{ ps}$) for compound **oc** and $k_{\rm CS} = 9 \times 10^{10} \text{ s}^{-1}$ ($\tau_{\rm CS} = 11 \text{ ps}$) for compound **oc2** (in CH₂Cl₂) leading to a short-lived charge-separated state consisting of the reduced perylene bisimide unit and the oxidized calix[4]arene moiety.

Introduction

Calixarenes are readily available supramolecular building blocks, which represent, next to the crown ethers¹ and the cyclodextrins,² the third generation of supramolecular host molecules. They consist of aromatic (arene) units (separated by methylene groups) that make up the walls of the chalice (calix)³ and are thus an ideal scaffold on which to assemble various desired functionalities such as nonlinear optical dyes,⁴ electrophores,⁵ and fluorophores.⁶ Their applications range from use as highly specific ligands for analytical chemistry and sensor techniques to applications in medical diagnostics. One of the most important properties of calix[4]arenes is, without doubt, their ability to include smaller molecules and ions reversibly. Accordingly, a variety of receptors for cations, anions, and neutral guests made from calix[4]arenes have been reported.⁷

Perylene bisimides (PBIs) represent important photo- and electro-active building blocks in supramolecular dye chemistry.^{8,9} Apart from their excellent emissive properties,¹⁰ their high absorption coefficients and photochemical stability and the fact that they are suitable for single-molecule spectroscopy¹¹ also make them highly promising candidates for molecular sensing applications.¹²

We recently reported calix[4]arene-perylene bisimide conjugates wherein both lifetimes and quantum yields of the attached perylene bisimide chromophores dramatically changed upon substitution to the calix[4]arene unit because of a fluorescence quenching process^{13,14} whereas the respective unsubstituted perylene bisimide chromophore shows a fluorescence quantum yield of about unity.8 Molecular systems in which photoinduced intramolecular electron transfer efficiently quenches the excited state of the chromophore form an important class of chemosensory materials.¹² Reactions with protons, metal ions, organic electrophiles, or surfaces are known to turn off the intramolecular electron transfer and to turn on fluorescence. One could accordingly think to reconstitute the original emission properties of the PBI chromophore within a calix[4]arene conjugate by means of complexation of a guest molecule into the calix[4] arene cavity which would, in this way, prevent the quenching process. However, prior to complexation studies, it is crucial to first understand the optical properties of the parent system and to get an in-depth picture of the primary photophysical processes taking place after photoexcitation.

Thus, we elucidate here the photophysical properties of an orange perylene bisimide chromophore (PBI) either substituted with one or two calix[4]arene moieties in the *N*-imide position. Also, the reference chromophore without calix[4]arene functionalization is investigated. The photoinduced processes are studied with time-resolved emission and femtosecond transient absorption spectroscopy. A quantitative analysis of the photophysical processes as well as their rates have been obtained by means of UV/vis absorption, steady-state and time-resolved emission, femtosecond transient absorption spectroscopy, spectrotemporal analysis of the femtosecond transient absorption data, and a theoretical analysis of the energetics of the processes.

^{*} Corresponding authors. E-mail: williams@science.uva.nl (R.M.W.) and wuerthner@chemie.uni-wuerzburg.de (F.W.).

[†] Universität Würzburg.

[‡] Vrije Universiteit.

[§] University of Trieste.

[&]quot;Universiteit van Amsterdam.

SCHEME 1: Synthetic Route and Chemical Structures of PBI-calix[4]arene Arrays and Reference Compounds Studied^{*a,b*}



^{*a*} Reagents and conditions: (a) **oPBA**, Zn(OAc)₂, quinoline, 160 °C, yield 28%; (b) **oPMI**, Zn(OAc)₂, quinoline, 165 °C, yield 85%. ^{*b*} For details on the synthesis of compound **oc2**, see ref 14.

TABLE 1: Optical Properties in CH₂Cl₂ (unless Indicated Otherwise)^a

UV/vis absorption			fluorescence emission						
compd	λ_{\max} (nm)	$\epsilon (M^{-1}cm^{-1})$	λ_{\max} (nm)	$\Phi_{\rm fl}$ toluene	$\begin{array}{c} \Phi_{fl} \\ CH_2Cl_2 \end{array}$	$\Phi_{ m fl}$ benzonitrile	τ (ns) toluene	τ (ns) CH ₂ Cl ₂	τ (ns) benzonitrile
oref	527	93600	534	$\sim 1.00^{b}$	0.99	$\sim 1.00^{b}$	4.0	4.9	3.9
ос	526	91600	535	0.02	0.03	0.02	с	с	С
$\mathbf{oc}2^d$	526	97200	532	< 0.01	< 0.01	< 0.01	С	с	С

^{*a*} All spectra recorded at room temperature. ^{*b*} $\Phi_{FI} \pm 0.02$. ^{*c*} Values could not be determined as the signal falls into the time response of the instrument of ca. 150 ps. ^{*d*} See ref 14.

The chemical structures of the compounds studied are shown in Scheme 1. Accordingly, one compound containing one calix-[4]arene unit (**oc**), one compound containing two calix[4]arene units (**oc2**), and the reference system containing no calix[4]arene units (**oref**) have been studied.

Results and Discussion

Synthesis and Structural Characterization. The studied perylene bisimide–calix[4]arene arrays were synthesized according to Scheme 1. For this purpose, two equivalents of 5-monoamino-25,26,27,28-tetrakis(propyloxy)-calix[4]arene were reacted with the orange perylene bisanhydride (**oPBA**) to yield the biscalix[4]arene-substituted perylene bisimide compound **oc2.** The imidization was carried out in quinoline at 160 °C, using Zn(OAc)₂ as a catalyst. Upon reaction of one equivalent of 5-monoamino-25,26,27,28-tetrakis(propyloxy)-calix[4]arene with the **orange** perylene monoimide (**oPMI**) in quinoline, the monocalix[4]arene-substituted compound **oc** was obtained (imidisation at 165 °C, catalyst Zn(OAc)₂). Both products were purified by column chromatography (SiO₂) and were characterized by ¹H NMR spectroscopy and high-resolution mass spectrometry.

Single crystals of **oc2** suitable for an X-ray analysis could be obtained by slow crystallization from chloroform/methanol at room temperature. Figure 1 shows the molecular structure and a view of the crystal packing of **oc2**, revealing a herringbone arrangement of the molecules. The crystal packing does not show any $\pi - \pi$ stacking of the pervlene units, and no solvent molecules are included in the crystal. The molecule has a pseudo-2/m symmetry with the twofold axis passing almost normally to the perylene moiety. Two calix[4]arene residues at the N-imide are oriented almost orthogonal on opposite sides of the plane dissecting the perylene chromophore. The PBI exhibits a flat π system, being ± 0.10 Å the maximum deviation of atoms from their mean plane. The calix[4]arene units are found in a pinched cone conformation. The dihedral angles formed by the C26/C28 and C25/C27 rings are of 11.8 and 80.3° (mean values), and correspondingly, the C26-C28 and C25-C27 distances are 4.52(3) and 9.77(4) Å, respectively. The dihedral angles between the calix[4]arene phenyl rings of the calix[4]arene and a "reference plane" passing through the four CH₂-methylene bridges of the calix[4]arene are 40.8(6)° for the phenyl ring containing the carbon atom C25 (phenyl rings are indicated by C label; see Figure 1), 89.5(4), 39.1(6), and 78.0-(4)° for the phenyl unit containing the carbon atom C26, C27, and C28, respectively. The corresponding values measured in the other calix[4]arene moiety are 43.4(7), 82.1(4), 37.5(6), and 86.8(4)° for ring 25a, 26a, 27a and 28a, respectively. The conformation of the calix[4]arene units with respect to the perylene is provided by the torsion angles around the N1-C25 and N2-C25a bonds. The calculated values are -111.7(19)° (C30-N1-C25-C17), 74.9(19)° (C30-N1-C25-C18), 65-(2)° (C34-N1-C25-C17) and -108.9(18)° (C34-N1-C25-



Figure 1. Top: Molecular structure of **oc2** in the crystalline state (H atoms omitted for clarity, only number of relevant C atoms indicated). Bottom: View of the packing of **oc2** in the crystal.



Figure 2. UV/vis absorption (solid line) and fluorescence emission spectra (dashed line) of compound **oc** in CH_2Cl_2 .

C18). The analogous data in the other unit are 107(2), $-58(4)^{\circ}$ and 118(3), $-77(3)^{\circ}$.

Optical Properties. All compounds were studied by UV/vis absorption and steady-state fluorescence spectroscopy in CH₂Cl₂. Their photophysical properties are summarized in Table 1, and the UV/vis absorption and fluorescence emission spectra of compound **oc** in CH₂Cl₂ are exemplarily depicted in Figure 2. The absorption spectra of both the two calix[4]arene-substituted compounds **oc** and **oc2** show the characteristic maxima of the perylene bisimide chromophore with bands at 526 and 490 nm (for both compounds **oc** and **oc2**, respectively). The calix[4]arene moiety absorbs only in the UV, with maxima at 280 and 288 nm.^{3b} Notably, solutions of the two compounds



Figure 3. Cyclic voltammogram in CH₂Cl₂ of compound **oc**, concentration = 1.0×10^{-4} M. Scan rate 100 mV s⁻¹. Working electrode: Pt disc, Ø 1 mm. Auxiliary electrode: Pt wire. Reference electrode: Ag/AgCl. Supporting electrolyte: TBAHFP (0.1 M).

oc and oc2 exhibit almost no fluorescence (for fluorescence quantum yields, see Table 1), whereas without calix[4]arene substituents, the orange perylene bisimide reference compound oref belongs to one of the most efficient fluorophores with a fluorescence quantum yield of about unity.8 This behavior is also observed for the values for the fluorescence quantum yields in the less polar solvent toluene and the more polar solvent benzonitrile (Table 1). It can be noted that the emission intensity of oc2 (which is on the edge of our instrumental limits) is clearly more strongly reduced than that of oc. The fluorescence emission data thus indicate an additional process taking place for both arrays oc and oc2 that strongly quenches the perylene bisimide emission upon attachment of the calix[4]arene moiety, and that is apparently independent of the solvent polarity. Thus, the electron-rich calix[4]arene acts as a fluorescence quencher for the electron-poor PBI chromophore.

Furthermore, the fluorescence lifetimes of all compounds have been determined in toluene, CH2Cl2, and benzonitrile, respectively, and the obtained values are summarized in Table 1. For the reference compound oref, a lifetime value of 4.9 ns is found in CH₂Cl₂, which is in reasonable agreement with the value of $\tau = 3.7$ ns reported in the literature for a similar compound in CHCl₃.^{8,10} For the fluorescence lifetime of compound oref in toluene, a value of $\tau = 4.0$ ns and in benzonitrile of $\tau = 3.9$ ns has been obtained. In contrast, for the orange calix[4]arenesubstituted PBI compounds oc and oc2, drastically quenched fluorescence lifetimes compared with the value of compound oref are found for all three solvents; the observed lifetime values for both oc and oc2 are lower than the system response time of approximately 150 ps. Apparently, the lifetime of both the orange systems is strongly shortened upon attachment of one or two calix[4]arene substituents. The changes in the fluorescence lifetimes upon attachment of one or two calix[4]arene units to the respective orange PBI chromophore thus relate to the observations made for the fluorescence quantum yields.

Electrochemistry and Spectro-electrochemistry. Compound oc was investigated by cyclic voltammetry in CH₂Cl₂ (vs Fc/ Fc⁺); the obtained cyclic voltammogram (CV) is shown in Figure 3, and the respective data are summarized in Table 2. Two reversible reduction bands at -1.01 V and -1.32 V (vs Fc/Fc⁺ couple) are observed for compound oc that can be attributed to the radical monoanion and dianion formation of the perylene bisimide chromophore.⁹ The first irreversible oxidation wave is found at +1.10 V for compound oc. This process cannot be attributed to the perylene bisimide unit whose oxidation is known to occur at higher voltage.⁹ When examining the CV of the plain tetrapropyloxy-calix[4]arene bearing no

	<i>E</i> _{red} (PBI ⁻ /PBI ²⁻)	$E_{\rm red}$ (PBI/PBI ⁻)	$E_{\rm ox}$ (PBI/PBI ⁺)	Onset of irrev. oxidation
oc	-1.32	-1.01	n. det. ^b	+1.10
oref ^a	-1.24	-1.01	+1.29	

^{*a*} See ref 9. ^{*b*} Value could not be determined owing to the irreversible oxidation process of the calix[4]arene moiety.



Figure 4. Spectro-electrogram of compound **oref** in CH_2Cl_2 with TBAHFP (0.1 M) as supporting electrolyte. Working electrode: Pt disc, \emptyset 6 mm. Auxiliary electrode: gold covered metal (V2A) plate. Reference electrode: Ag/AgCl. Arrows indicate the spectral changes upon stepwise decrease of the applied potential leading to formation of the respective radical monoanionic perylene species.

substituents, a similar irreversible feature above +1.15 V is observed (see Supporting Information). Furthermore, for methoxybenzene, which serves as a reference compound for the attached calix[4]arene moiety, an oxidation potential of +1.24 V (recalculated from +1.76 V vs SCE, value in CH₃CN)¹⁶ is found in the literature which is in reasonable agreement with our values for compound **oc**. The irreversible oxidation features observed in the CV of compound **oc** are thus assigned to the oxidation of the calix[4]arene moiety (further on referred to as E_{ox} (Calix)). The reduction potential found for the perylene bisimide unit E_{red} (PBI) closely resemble the values reported in the literature for the reference compound **oref** without calix-[4]arene moieties (see Table 2).^{8,9}

The monoreduced state of compound **oref** was characterized by spectro-electrochemistry in CH_2Cl_2 ; the respective spectroelectrogram is depicted in Figure 4. The monoanionic species shows absorption maxima at 713, 800, and 955 nm which are in good agreement with the values reported in the literature.¹⁷

Gibbs Energy of Photoinduced Electron Transfer. As discussed above, in the cyclic voltammograms of compound oc an irreversible wave around +1.10 V was observed that was attributed to the oxidation of the calix[4]arene moiety. To further examine the feasibility of a photoinduced charge separation, it is instructive to consider the thermodynamics of such a process. Therefore, the Gibbs free energy of an intramolecular chargeseparated state ($\Delta G_{\rm CS}$) in a covalently bonded donor-acceptor system was calculated for compound oc using eq 1, where $E_{\rm ox}({\rm Calix})$ represents the value for the first oxidation potential of the calix[4] arene moiety, E_{red} (PBI) denotes the first reduction potential of the PBI acceptor, E_{00} is the energy of the $S_1 \rightarrow S_n$ excited state, $R_{\rm CC}$ refers to the distance between the centers of the donor and acceptor segments, r^+ and r^- represent the effective ionic radii of the donor and acceptor radical cation and anion, respectively, ϵ_{ref} denotes the reference solvent dielectric constant used in electrochemistry, and ϵ_S is the respective solvent dielectric constant:18

$$\Delta G_{\rm CS} = e[E_{\rm ox}({\rm Calix}) - E_{\rm red}({\rm PBI})] - E_{00} - \frac{e^2}{4\pi\epsilon_0\epsilon_S R_{\rm CC}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r^+} + \frac{1}{r^-}\right) \left(\frac{1}{\epsilon_{\rm ref}} - \frac{1}{\epsilon_S}\right) (1)$$

To calculate $\Delta G_{\rm CS}$ according to eq 1, the first reduction potential $E_{red}(PBI)$ of compound oc (for values see Table 2) in CH₂Cl₂ ($\epsilon_{\rm S} = 8.93$) was used, and $E_{\rm ox}({\rm Calix}) = +1.10 {\rm V}$ was estimated from the onset of the irreversible oxidation of the tetrapropyloxy-calix[4]arene unit in Figure 3 (see also Supporting Information). The distance between the centers of the donor and acceptor segments $R_{\rm CC}$ was estimated from an energy minimized structure (see Supporting Information) to be $R_{\rm CC} = 8.60$ Å for compound **oc**. All electrochemical values were obtained in CH₂Cl₂, and therefore ϵ_{ref} equals ϵ_s ; thus, the last solvent related term in eq 1 vanishes. Substitution of all remaining parameters shows that the energy of the intramolecular charge-separated state in CH₂Cl₂ is lower than the energy of the respective $S_1 \rightarrow S_n$ excited state for compound oc (E_{00} = 2.34 eV). The thus estimated value for $\Delta G_{\rm CS} = -0.418$ eV shows that electron transfer from the calix[4]arene substituent to the photo-excited perylene bisimide moiety in compound oc is an exergonic reaction in CH2Cl2. Therefore, it can be concluded that the creation of a charge-separated state consisting of the radical cation of the calix[4]arene moiety and the radical anion of the perylene unit is energetically feasible for compound oc. Thus, the strongly decreased fluorescence quantum yields and lifetimes for the orange systems oc and oc2 upon attachment of one or two calix[4]arene moieties compared with the orange reference compound oref should be most likely attributed to a rapid photoinduced electron-transfer process.

Femtosecond Transient Absorption Spectroscopy. To shed more light on this quenching process, all compounds were investigated with femtosecond transient absorption spectroscopy in toluene, CH₂Cl₂, and benzonitrile solution. The spectral data obtained in toluene for compounds oc, oc2, and oref are shown in Figure 5 (for all other spectra, see Supporting Information). For all three compounds upon photoexcitation, an intense bleaching due to the depopulation of the ground state molecules in the probe area is observed at both 530 and 490 nm. These bands are related to the $S_0 \rightarrow S_1$ transitions of the orange PBI chromophore. Furthermore, an intense negative signal is present in all spectra of oc, oc2, and oref at around 530 and 580 nm which can be assigned to the stimulated emission of the orange PBI chromophore. These features are accompanied by a strong positive absorption band with a maximum centered at 700 nm for both compounds. The latter was assigned to the $S_1 \rightarrow S_n$ absorption of the orange perylene (absorption maximum of compound oref at 695 nm in toluene, see Figure 5). It is noteworthy, however, that the radical anion of oref also absorbs at 700 nm (see Figure 4). When changing to the more polar solvent CH₂Cl₂, for all three compounds oref, oc, and oc2, the negative bands at 490, 530, and 580 nm, respectively, remain unchanged. However, the maximum of the strong positive absorption band is shifted from 695 nm in toluene to 715 nm in CH₂Cl₂ (for spectra see Supporting Information). The femtosecond transient absorption spectra in benzonitrile show negative bands at 495, 535, and 585 nm and a broad, positive absorption band at 735 nm (for spectra see Supporting Information). The negative bands are thus bathochromically shifted by about 5 nm compared with the band positions found in toluene and CH₂Cl₂, whereas the positive absorption band appears bathochromically shifted by 20 nm compared with that of CH₂Cl₂.



Figure 5. Femtosecond transient absorption spectra and corresponding time delays in toluene after photoexcitation at 530 nm. Top: compound oc. Middle: compound oc2. Bottom: compound oref. For compound oc2, the scattered laser pulse is observed.

Global and Target Analysis. The kinetic profiles of the observed photoinduced processes are difficult to analyze by single wavelength fitting because several processes take place concomitantly after photoexcitation. For this reason, the femtosecond transient absorption data matrices in toluene, CH₂Cl₂, and benzonitrile were analyzed with spectrotemporal parametrization, an advanced global and target analysis method that has been developed, in particular, to elucidate photoinduced processes in complex biological systems such as photosystems.¹⁹ Here, "global" refers to a simultaneous analysis of all measurements, whereas "target" refers to the applicability of a particular target model (see below). Because the time information at all wavelengths is analyzed, this analysis gives a more in-depth

view of the occurring photoinduced processes. For this purpose, all time-gated spectra are collected in a matrix, which was globally fitted applying a sequential kinetic scheme with increasing lifetimes. This procedure yields the evolutionassociated difference spectra (EADS), the spectra of the individual excited-state species, together with their respective rate constants. The EADS thus represent the spectral evolution of the excited-state species. However, in the EADS, the time constants of the processes may correspond to the lifetimes of the transient species, but the spectral profiles do not necessarily need to represent the pure excited-state spectra of the molecules: given the fact, that the applied sequential scheme with increasing lifetimes represents the correct physicochemical picture, the EADS indeed correspond to the true spectra of the individual excited-state species characterizing the intermediate states. These "true spectra" are also referred to as species associated difference spectra (SADS) and will in this case be identical to the EADS. However, for more complex systems following nonsequential kinetic schemes, the EADS will not truly reproduce the spectra of the individual excited species, and EADS and SADS will differ substantially. To obtain the correct SADS (= the correct difference spectra of the individual species), a target analysis needs to be applied. Thus, one needs to take into account additional (e.g., experimentally based) parameters that are summarized into a specific photophysical or photochemical model utilized for the fitting procedure.

In case of compound oc, the EADS resulting from the global fit of the data obtained in toluene are presented in Figure 6. Three decay components of 1.8, 22, and 50 ps are observed. The very first lifetime we assume to be due to fast solvent reorganization processes.^{20,21} The EADS corresponding to this component is shown as a green line in Figure 6A; it closely resembles the features typical for the transient absorption spectrum of the orange PBI chromophore (for comparison, see spectra of compound oref in Figure 5). With a representative time of 1.8 ps, this spectrum is converted into an EADS with a lifetime of 22 ps (black line in Figure 6A) showing a loss of amplitude in the negative bands at 530 and 580 nm, whereas the amplitude remains almost unchanged at the ground-state bleaching band of 490 nm and the absorption band of approximately 700 nm, characteristic of the solvation effect. The spectrum of the third component (red line in Figure 6A) is obtained during further evolution of the system, this EADS decays with 50 ps. The spectrum very strongly suggests the formation of a different excited state, as the almost complete loss of stimulated emission at 580 nm is observed, together with a broadening and apparent blue shift of the positive transient absorption band around 700 nm.

Although the sequential model used above for fitting of the data provides important information on the time evolution of the system, it cannot truly reproduce the spectra of the individual excited species that are involved in the processes occurring in compound oc upon photoexcitation. Therefore, a target analysis with a specific model of the excited-state processes was applied: according to the calculations of the Gibbs energy of electron transfer as well as the observed trends in the fluorescence lifetimes and quantum yields (vide supra), the formation of the PBI radical anion of the orange PBI chromophore is expected after photoexcitation of compound oc as a result of a photoinduced electron transfer of the excited singlet state of compound oc. Accordingly, an additional charge-transfer (CT) state was integrated into the model. The respective energy level diagram is depicted in Figure 7. The resulting SADS, now representing the true spectra of the individual excited species,



Figure 6. Compound **oc** in toluene. A (top): evolution-associated difference spectra (EADS) resulting from the global fitting analysis of femtosecond transient absorption data. Features due to Raman scattering were omitted for clarity. B (bottom): species-associated difference spectra (SADS) resulting from the simultaneous target analysis of femtosecond transient absorption data of compounds **oc** and **oc2** using the kinetic scheme depicted in Figure 7.²² Shown are processes after photoexcitation at 530 nm. The black SADS represents the excited-state **o*c**, and the red SADS belongs to the **oc** CT state.



Figure 7. Energy level diagram of compound **oc** in toluene showing the electron-transfer pathway obtained with global and target analysis, together with the respective decay times corresponding to the states.^{22,23}

are shown in Figure 6B.²² The SADS of the excited state (black line in Figure 6B) shows again the transient absorption features of the orange PBI chromophore and decays with 25 ps (80%) and with 2 ps (20%),²³ respectively, to the following state (red line). The SADS of the latter shows a lifetime of 53 ps and exactly reveals the spectral features of a charge-transfer state, as the stimulated emission at 580 nm is not observed any longer and the band at around 700 nm is significantly broadened. From this clear spectral evidence, the formation of a charge-separated



Figure 8. Kinetic profiles of the transient absorption of compound **oc** in toluene. Top: the decay of the ground state bleaching measured at 485 nm (red line) and the decay of the stimulated emission at 580 nm (black line). Bottom: the rise and decay time of the CT state measured at 635 nm (red line) and the concomitant decay of CT state and $S_1 \rightarrow S_n$ absorption at 700 nm (black line).

state involving the formation of the orange PBI monoanion can be concluded.

The formation of the CT state is furthermore illustrated by the kinetic traces presented in Figures 8 and 9: a clear difference is found when comparing the decay of the ground state bleaching (probed at 485 nm) and that of the stimulated emission (probed at 580 nm), respectively (see Figure 8, top). It can be seen clearly, that the signal of the stimulated emission vanishes much faster than that of the ground state bleaching. Thus, the ground state is still bleached when no emission occurs any more from the excited singlet state by stimulated emission. Accordingly, an additional, nonemissive state (i.e., a CT state) is populated during the photoexcitation process. Furthermore, the kinetic profile measured at 635 nm in Figure 8 (bottom) shows a clear rise time. At this very wavelength the charge-transfer state absorbs almost exclusively (see red line in Figure 6B), as the $S_1 \rightarrow S_n$ absorbance of the excited state equals zero, and the time-resolved trace at this wavelengths thus resembles the time course of the CT state concentration. In comparison, the kinetic profile probed at 700 nm shows no such clearly pronounced rise time, as both the decay of the $S_1 \rightarrow S_n$ absorption and the rise and decay of the CT state, respectively, are concomitantly observed at this wavelength. Note, that the fit of the data (dashed lines in Figure 9) is excellent. Figure 9 depicts the kinetics of the oc and oc2 systems (lines in black and red, respectively). Note that in toluene (left panel) the faster charge separation in oc2 is clearly visible as a faster decay of the stimulated emission (probed at 580 nm) and as a faster rise of the 631 nm signals (radical anion absorption). Note further that in benzonitrile (right panel) the inverse kinetics is visible: the CT state absorption (probed at 631 nm) decays with apparently the same lifetime



Figure 9. Selected traces and fits (dashed lines) of transient absorption of compound **oc** (black) and **oc2** (red) in toluene (left) and benzonitrile (right). The decay of the ground state bleaching measured at 485 nm and the decay of the stimulated emission at 582 nm; the rise and decay time of the CT state measured at 635 nm and the concomitant decay of CT state and $S_1 \rightarrow S_n$ absorption at 700 nm. Note that the time axis is linear up to 1 ps and is logarithmic thereafter.

TABLE 3: Lifetimes for Charge Separation (τ_{CS}) and Charge Recombination (τ_{CR}) Obtained from the Simultaneous Target Analysis of Compounds oc and oc2 in Various Solvents (Estimated Relative Error 10%)

compd	solvent	$ au_{\mathrm{CS}^{a}}(\mathrm{ps})$	$\tau_{\rm CR}$ (ps)
oc	toluene	25	53
	CH_2Cl_2	32	10
	benzonitrile	64	15
oc2	toluene	11	53
	CH_2Cl_2	11	10
	benzonitrile	24	15

^a See refs 23 and 24.

as the stimulated emission, and the ground state bleaching (probed at 485 nm) decays faster in **oc2** than in **oc** (even under the imposed identical lifetime of the CT state). Detailed analysis of the late time gated spectra reveals that a very small amount ($\leq 2\%$) of triplet is created.

Similar processes are observed in the spectra of compounds oc and oc2 measured in the other two solvents, CH₂Cl₂ and benzonitrile; the respective SADS are depicted in the Supporting Information. However, the charge-transfer character of the charge-separated states of the two compounds is less pronounced than that in toluene because of the much faster decay of this state. To further analyze this phenomenon, for all femtosecond transient absorption data obtained in all three solvents for both compounds, oc and oc2, respectively, again, a target analysis has been applied. The obtained values for the rates of charge separation and charge recombination in the various solvents are collated in Table 3. The values for charge separation reveal for compound oc values of 25 ps (in toluene), 32 ps (in CH₂Cl₂), and 64 ps (in benzonitrile).²⁴ The charge recombination after photoinduced charge separation within the system oc occurs with 53 ps in toluene.^{23,24} This value lowers to 10 ps when changing to the more polar solvent CH2Cl2 and also shows a reduced value of 15 ps in benzonitrile.^{23,24} Similar trends in the rate constants are observed for the biscalix[4]arene-substituted compound oc2 (see Table 3).²⁴ Accordingly, values for the charge separation for compound oc2 of 11 ps (in toluene), 11 ps (in CH₂Cl₂), and 24 ps (in benzonitrile) are obtained, respectively,²⁴ and charge recombination values of 53 ps in toluene, of 10 ps in the more polar CH₂Cl₂ and of 15 ps in benzonitrile were determined, respectively. Hence, the lifetime values for charge separation are lower in toluene (25 ps in oc and 11 ps in oc2, respectively) and increase in the more polar solvents CH₂Cl₂ (32 ps in oc and 11 ps in oc2) and benzonitrile (64 ps in oc and 24 ps in oc2). Thus, remarkably, charge separation in oc and oc2 occurs faster in the less polar solvent toluene and slower in the more polar solvents CH₂Cl₂ and benzonitrile despite the larger driving force in the latter.²⁵ Furthermore, the lifetime values reduce approximately by half for compound oc2 compared with those obtained for compound oc in the respective solvent, owing to the presence of two electron-transfer channels for deactivation in compound oc2 due to bis-calix[4]arene substitution of the PBI chromophore. Accordingly, a value of $\tau_{CS} = 11$ ps is observed for compound **oc2** in toluene compared with a value of $\tau_{\rm CS} = 25$ ps found for compound oc, and also values of $\tau_{\rm CS} = 11$ ps (for compound oc2) compared with $\tau_{CS} = 32$ ps (for compound oc) in CH₂Cl₂ and values of $\tau_{\rm CS} = 24$ ps (for compound oc2) compared with $\tau_{\rm CS} = 64$ ps (for compound oc) in benzonitrile were determined (see Table 3). In the more polar solvents CH₂Cl₂ and benzonitrile, the charge-separated state will be lower in energy and therefore thermodynamically more stabilized. As a consequence, this leads to faster recombination rates which may be attributed to the energy-gap law^{12b} or to increased overlap of vibrational wavefunctions in the Marcus inverted region. Similar behavior has also been observed previously in other electron donoracceptor systems.²⁶ Increase in solvent polarity results in an increase of the driving force for photoinduced charge separation. Consequently, the driving force for charge recombination becomes smaller. Because of the fact that charge recombination is normally in the Marcus inverted region, the process becomes faster with the increase of the polarity of the solvent.²⁵

The data analysis for both calix[4]arene—perylene bisimide conjugates clearly revealed the formation of a charge-separated state, involving the formation of the radical anion of the orange perylene bisimide chromophore. Owing to this process, the excited-state lifetime is strongly reduced from approximately 4 ns to around 65 ps and less. The charge-transfer state is clearly characterized by the absence of stimulated emission and the broadened absorption features in the 600 - 750 nm spectral region attributable to the radical anion of the perylene bisimide unit (see Figure 4 for comparison). Concomitantly, the radical cation of calix[4]arene (i.e., dimethyl substituted methoxybenzene) should be formed. This radical cationic species, however, is expected to absorb mainly in the UV and with a very small extinction coefficient and thus could not be observed in the spectra.

Conclusions

Calix[4]arene functionalization does substantially influence the properties of the important perylene bisimide fluorophore. A charge-separated state is formed, consisting of the reduced perylene bisimide unit and the oxidized calix[4]arene moiety. As a consequence, the excited-state lifetime is strongly reduced from around 4 ns to less than 65 ps. The resulting charge-transfer state is characterized by ground state bleaching, the absence of stimulated emission and absorption features in the 600 – 750 nm region attributable to the radical anion of the perylene bisimide. We assume that the closest substituted methoxybenzene of the calix[4]arene acts as the donor, and thus, the radical cation of (dimethyl substituted) methoxybenzene should be formed. These findings demonstrate the sensitivity of perylene bisimides to the local environment that makes them attractive for calix[4]arene-based fluorescence sensors which we will further elaborate on in the future toward sensing and molecular recognition applications. Furthermore, our study exemplifies that global and target analysis is a strong tool to elucidate competing processes involving excited-state species with similar absorption properties. Thus, spectrotemporal parametrization is the tool of choice for the investigation of complex multichromophoric supramolecular and biological assemblies.

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Supporting Information Available: Synthetic and experimental details, molecular modeling structures, electrochemical data, femtosecond transient absorption spectra as well as data obtained from global and target analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Pedersen, C. J. J. Am. Chem. Soc. 1967, 89, 7017-7036.

(2) Cyclodextrin Chemistry; Bender, M. L., Komiyama, M., Eds.; Springer: Berlin, 1978.

(3) (a) *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001. (b) *Calixarenes*; Gutsche, D. C., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1993. (c) *Calixarenes Revisited*; Gutsche, D. C., Ed.; The Royal Society of Chemistry: Letchworth, 1998. (d) Böhmer, V.; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713–745.

(4) Kenis, P. J. A.; Noordman, O. F. J.; Houbrechts, S.; van Hummel, G. J.; Harkema, S.; van Veggel, F. C. J. M.; Clays, K.; Engbersen, J. F. J.; Persoons, A.; van Hulst, N. F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 7875–7883.

(5) Zhao, B.-T.; Blesa, M.-J.; Mercier, N.; Le Derf, F.; Sallé, M. J. Org. Chem. 2005, 70, 6254–6257.

(6) (a) Schazmann, B.; Alhashimy, N.; Diamond, D. J. Am. Chem. Soc. **2006**, *128*, 8607–8614. (b) Souchon, V.; Leray, I.; Valeur, B. *Chem. Commun.* **2006**, 4224–4226. (c) Lee, S. H.; Kim, S. H.; Kim, S. K.; Jung, J. H.; Kim, J. S. *J. Org. Chem.* **2005**, *70*, 9288–9295. (d) Kim, S. K.; Bok, J. H.; Bartsch, R. A.; Lee, J. Y.; Kim, J. S. *Org. Lett.* **2005**, *7*, 4839–4842. (e) Kim, S. K.; Lee, S. H.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. J. Am. Chem. Soc. 2004, 126, 16499-16506. (f) Leray, I.; Lefevre, J.-P.; Delouis, J.-F.; Delaire, J.; Valeur, B. Chem.-Eur. J. 2001, 7, 4590-4598. (g) van der Veen, N.; Flink, S.; Deij, M. A.; Egberink, R. J. M.; van Veggel, F. C. J. M.; Reinhoudt, D. N. J. Am. Chem. Soc. 2000, 122, 6112-6113. (h) Ji, H.-F.; Dabestani, R.; Brown, G. M.; Sachleben, R. A. Chem. Commun. 2000, 833-834. (i) Ji, H.-F.; Brown, G. M.; Dabestani, R. Chem. Commun. 1999, 609-610. (j) Jin, T.; Chem. Commun. 1999, 2491-2492. (k) Larey, I.; O'Reilly, F.; Habib Jiwan, J.-L.; Soumillion, J.-P.; Valeur, B. Chem. Commun. 1999, 795-796. (1) Beer, P. D.; Timoshenko, V.; Maestri, M.; Passaniti, P.; Balzani, V. Chem. Commun. 1999, 1755-1756. (m) Unob, F.; Asfari, Z.; Vicens, J. Tetrahedron Lett. 1998, 39, 2951-2954. (n) Jin, T.; Monde, K. Chem. Commun. 1998, 1357-1358. (o) Ikeda, A.; Yoshimura, M.; Lhotak, P.; Shinkai, S. J. Chem. Soc., Perkin Trans. 1, 1996, 1945-1950. (p) Grigg, R.; Holmes, J. M.; Jones, S. K.; Norbert, W. D. J. A. J. Chem. Soc., Chem. Commun. 1994, 185-187. (q) Aoki, I.; Sakaki, T.; Shinkai, S. J. Chem. Soc., Chem. Commun. 1992, 730-732. (r) Jin, T.; Ichikawa, K.; Koyama, T. J. Chem. Soc., Chem. Commun. 1992, 499-501.

(7) 7) (a) Calixarenes in Action; Mandolini, L., Ungaro, R., Eds.; Imperial College Press: London, 2000. (b) Schazmann, B.; O'Malley, S.; Nolan, K.; Diamond, D. Supramol. Chem. 2006, 18, 515-522. (c) Lemli, B.; Peles, J.; Kollár, L.; Nagy, G.; Kunsági-Máté, S. Supramol. Chem. 2006, 18, 251-256. (d) Rozhenko, A. B.; Schoeller, W. W.; Letzel, M. C.; Decker, B.; Agena, C.; Mattay, J. Chem.-Eur. J. 2006, 12, 8995-9000. (e) Eckel, R.; Ros, R.; Decker, B.; Mattay, J.; Anselmetti, D. Angew. Chem., Int. Ed. **2005**, *44*, 484–488. (f) Ji, H.-F.; Dabestani, R.; Brown, G. M. *J. Am. Chem. Soc.* **2000**, *122*, 9306–9307. (g) Kim, J. S.; Shon, O. J.; Ko, J. W.; Cho, M. H.; Yu, I. Y.; Vicens, J. *J. Org. Chem.* **2000**, *65*, 2386–2392. (h) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713–1734. (i) Diamond, D.; McKervey, M. A. *Chem. Soc. Rev.* **1996**, 15–24.

(8) Würthner, F. Chem. Commun. 2004, 1564-1579.

(9) You, C.-C.; Dobrawa, R.; Saha-Möller, C. R.; Würthner, F. Top. Curr. Chem. 2005, 258, 39-82.

(10) Ford, W. E.; Kamat, P. V. J. Phys. Chem. 1987, 91, 6373-6380.
(11) (a) De Schryver, F. C.; Vosch, T.; Cotlet, M.; Van der Auweraer, M.; Müllen, K.; Hofkens, J. Acc. Chem. Res. 2005, 38, 514-522. (b) Zang, L.; Liu, R.; Holman, M. W.; Nguyen, K. T.; Adams, D. M. J. Am. Chem. Soc. 2002, 124, 10640-10641. (c) Sauer, M. Angew. Chem., Int. Ed. 2003, 42, 1790-1793.

(12) (a) Supramolecular Photochemistry; Balzani, V., Scandola, F., Eds.;
Ellis Horwood: Chichester, U.K., 1991. (b) Modern Molecular Photochemistry; Turro, N. J., Ed.; University Science Books: Sausalito, CA, 1991. (c) Fundamentals of Photoinduced Electron Transfer; Kavarnos, G. J., Ed.; VCH Publishers Inc.: New York, 1993. (d) Electron Transfer in Chemistry; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vols. 1–5. (e) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. Coord. Chem. Rev. 2000, 205, 41–57. (f) Armaroli, N. Photochem. Photobiol. Sci. 2003, 2, 73–87. (g) Valeur, B.; Leray, I. Coord. Chem. Rev. 2000, 205, 3–40. (h) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. Chem. Rev. 1997, 97, 1515–1566. (i) Wasielewski, M. R. Chem. Rev., 1992, 92, 435–461. (j) Dirksen, A.; De Cola, L. C. R. Chim. 2003, 6, 873–882. (k) Guldi, D. M. Chem. Soc. Rev. 2002, 31, 22–36.

(13) Vysotsky, M. O.; Böhmer, V.; Würthner, F.; You, C.-C.; Rissanen, K. Org. Lett. **2002**, *4*, 2901–2904.

(14) Hippius, C.; Schlosser, F.; Vysotsky, M. O.; Böhmer, V.; Würthner,
 F. J. Am. Chem. Soc. 2006, 128, 3870–3871.

(15) Van der Boom, T.; Evmenenko, G.; Dutta, P.; Wasielewski, M. R. Chem. Mater. 2003, 15, 4068-4074.

(16) Zweig, A.; Hodgson, W. G.; Jura, W. H. J. Am. Chem. Soc. 1964, 86, 4124-4129.

(17) Ford, W. E.; Hiratsuka, H.; Kamat, P. V. J. Phys. Chem. 1989, 93, 6692-6696.

(18) Weller, A. Z. Phys. Chem. 1982, 133, 93-98.

(19) (a) van Stokkum, I. H. M.; Larsen, D. S.; van Grondelle, R. *Biochim. Biophys. Acta* **2004**, *1657*, 82–104. (b) van Stokkum, I. H. M.; Lozier, R. H. J. Phys. Chem. B **2002**, *106*, 3477–3485. (c) Mullen, K. M.; van Stokkum, I. H. M. J. Stat. Software **2007**, *18* (3); http://www.jstatsoft.org/ v18/i03/. (d) Global and target analysis can be performed with, e.g., the R package TIMP; see http://cran.r-project.org/doc/packages/TIMP.pdf.

(20) Schweitzer, G.; Gronheid, R.; Jordens, S.; Lor, M.; De Belder, G.; Weil, T.; Reuther, E.; Müllen, K.; De Schryver, F. C. J. Phys. Chem. A **2003**, *107*, 3199–3207.

(21) De Belder, G.; Jordens, S.; Lor, M.; Schweitzer, G.; De, R.; Weil, T.; Herrmann, A.; Wiesler, U. K.; Müllen, K.; De Schryver, F. C. J. Photochem. Photobiol. A **2001**, 145, 61–70.

(22) To quantify the differences between the rates of charge separation (k_{CS}) and charge recombination (k_{CR}) , we performed a simultaneous target analysis of compounds **oc** and **oc2**. The kinetic model used consists of a biexponential decay of the excited state to a charge-separated state, which in turn decays with k_{CR} . In order to limit the number of free parameters, the SADS of the excited state were assumed to be identical in **oc** and **oc2**. Thus, the difference between **oc** and **oc2** is quantified by the rates of slow (the dominant fraction) and fast charge separation (the minor fraction; see ref 23).

(23) A second minor deactivation pathway with 20% amplitude of the singlet excited state of compound **oc** is observed in toluene which is most probably related to the decay of a second possible pinched-cone conformation of the calix[4]arene moiety. As we are dealing here with merely conformational isomers, the additionally assumed species of this second pathway has identical spectral features and an indistinguishable depopulation pathway to the ground state.

(24) As discussed before (see ref 23), faster components are also observed for the data of compound oc in the solvents CH_2Cl_2 (7.7 ps, 32%) and benzonitrile (8.3 ps, 33%). These are again attributable to the second pinched-cone conformation of the calix[4]arene moiety. Likewise, for compound oc2 in all three solvents, a fast component showing a lifetime of <1 ps (20%) in toluene, 3.6 ps (32%) in CH_2Cl_2 , and 3.8 ps (33%) in benzonitrile is observed. Note that, again, the lifetimes of this faster component of compound oc2 reduce by half compared with those obtained for compound oc for the respective solvents owing to the availability of a second electron-transfer deactivation channel in compound oc2.

(25) For rare examples, for charge separation in the Marcus inverted region, see: (a) Mataga, N.; Chosrowjan, H.; Taniguchi, S.; Shibata, Y.;

Yoshida, N.; Osuka, A.; Kikuzawa, T.; Okada, T. *J. Phys. Chem. A* **2002**, *106*, 12191–12201. (b) Beckers, E. H. A.; Meskers, S. C. J.; Schenning, A. P. H. J.; Chen, Z.; Würthner, F.; Janssen, R. A. J. *J. Phys. Chem. A* **2004**, *108*, 6933–6937.

(26) (a) Asahi, T.; Ohkohchi, M.; Matsusaka, R.; Mataga, N., Zhang,
R. P.; Osuka, A; Maruyamat, K. J. Am. Chem. Soc. 1993, 115, 5665-

5614. (b) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771–11782. (c) Tan, Q.; Kuciauskas, D.; Lin, S.; Stone, S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. B* **1997**, *101*, 5214–5223. (d) Armaroli, N.; Accorsi, G.; Song, F.; Palkar, A.; Echegoyen, L.; Bonifazi, D.; Diederich, F. *ChemPhysChem* **2005**, *6*, 732–743.