

A Revisit to the Orthogonal Bodipy Dimers: Experimental Evidence for the Symmetry Breaking Charge Transfer-Induced Intersystem Crossing

Ya Liu,^{†,‡} Jianzhang Zhao,^{*,§} Alessandro Iagatti,^{||,⊥} Laura Bussotti,^{||} Paolo Foggi,^{||,⊥,#} Elena Castellucci,^{||} Mariangela Di Donato,^{*,||,⊥} and Ke-Li Han^{*,†}

[†]State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

[§]State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 West Campus, 2 Ling Gong Road, Dalian 116024, People's Republic of China

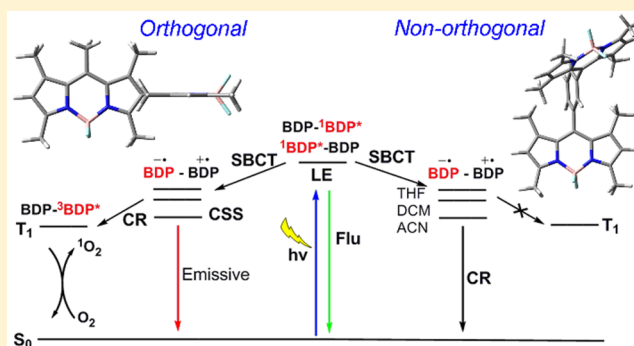
^{||}LENS (European Laboratory for Non-Linear Spectroscopy) via N. Carrara 1, 50019 Sesto Fiorentino, Italy

[⊥]INO, Istituto Nazionale di Ottica Largo Enrico Fermi 6, I-50125 Florence, Italy

[#]Dipartimento di Chimica, Università di Perugia, via Elce di Sotto 8, 06123 Perugia, Italy

S Supporting Information

ABSTRACT: A series of Bodipy dimers with orthogonal conformation were prepared. The photophysical properties were studied with steady-state and time-resolved transient spectroscopies. We found the triplet-state quantum yield is highly dependent on the solvent polarity in the orthogonally linked symmetric Bodipy dimers, and the intersystem crossing (ISC) is efficient in solvents with moderate polarity. The photoinduced symmetry-breaking charge transfer (SBCT) in polar solvents was confirmed by femtosecond transient absorption spectroscopy, with the charge separation (CS) kinetics on the order of a few picoseconds and the charge recombination (CR) process occurring on the nanosecond time scale in dichloromethane. These observations are supported by the calculation of the charge separated state (CSS) energy levels, which are high in nonpolar solvents, and lower in polar solvents, thus the CR-induced ISC has the largest driven force in solvents with moderate polarity. These results clarify the mechanism of SOCT-ISC in the orthogonally symmetric Bodipy dimers. The acquired information, relating molecular structure and ISC property, will be useful for devising new strategies to induce ISC in heavy atom-free organic chromophores.



1. INTRODUCTION

Triplet photosensitizers, or compounds which show efficient intersystem crossing (ISC) upon photoexcitation, are tremendously important concerning fundamental photochemistry (such as energy transfer and electron transfer),^{1,2} photoredox catalytic organic reactions,^{3,4} photodynamic therapy (PDT),^{5–7} and triplet–triplet-annihilation upconversions.^{8–10} Recently, orthogonal Bodipy dimers were reported to show moderate to excellent ISC ability. In this case no heavy atom effect is required, and the two Bodipy chromophores are symmetric and in an orthogonal geometry.^{11–18} It was initially proposed that the formation of a “doubly substituted” excited state was responsible for the efficient ISC observed in this kind of dimers.^{12,13} However, subsequent studies revealed that this phenomenon was solvent-dependent and the orthogonal geometry of the Bodipy dimers was crucial for the ISC.^{15,17,18} Recently, it has been proposed that charge recombination (CR)

is responsible for the ISC of these Bodipy dimers.^{16–19} CR-induced triplet-state formation is usually referred to as “photoinduced spin–orbital charge transfer enhanced ISC” (SOCT-ISC) which was used to induce triplet state in some donor–acceptor systems linked in orthogonal geometry and presenting efficient charge transfer from electron donor to acceptor in a mechanism that orbitals angular momentum change in CR will be compensated by the change of electron spin angular momentum.^{20–25} In this concept, a stable charge separation state (CSS) precursor and an orthogonal geometry are required. Excited state symmetry breaking charge transfer (SBCT) was observed in some chromophore dyads, including Bodipy dyads connected by covalent or coordination

Received: October 15, 2017

Revised: December 30, 2017

Published: January 16, 2018

bond.^{26–28} It was found that asymmetric fluctuations in the solvent shell are sufficient to induce SBCT in the energy of local excited state (LE) on a very short time scale (~ 10 ps), distributing LE state and CT state.²⁸

Herein we prepared several Bodipy dimers with orthogonal geometry and we confirmed the formation of a CSS upon photoexcitation. In polar solvents, an emission band ascribable to the presence of a CSS was observed, and the corresponding energy levels in different solvents were characterized by means of electrochemical and optical spectral data. Comparison of these energy levels with those of the singlet and triplet excited state was also made. Furthermore, we visualized the charge separation process with femtosecond transient absorption spectroscopy (fs TAS). The information obtained through this extended characterization provided a clear picture of the mechanism of SOCT-ISC process in the analyzed orthogonal symmetric Bodipy dimers.

2. EXPERIMENTAL SECTION

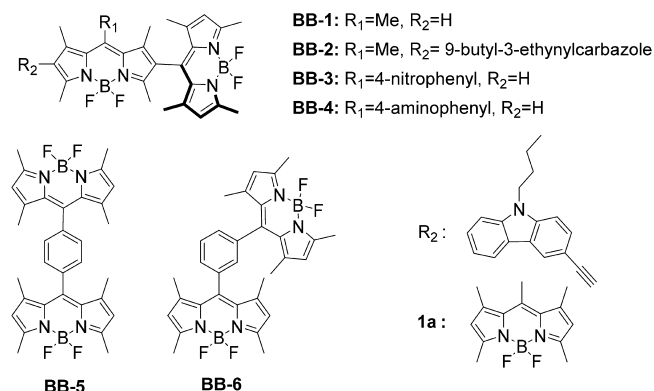
The synthesis and characterization of the Bodipy dimers described here are reported in the [Supporting Information](#) (SI) section. XRD measurements of **BB-3** and **BB-5** were performed on an X'pert PRO diffractometer equipped with Cu K X-ray ($\lambda = 1.54186$ Å) tubes. UV–vis absorption spectra were registered on a HP8453 UV–vis spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorometer. Luminescence lifetimes were measured on an OB920 fluorescence/phosphorescence lifetime instrument (Edinburgh, U.K.). Nanosecond transient absorption spectra were recorded on a LP920 Spectrometer (Edinburgh, U.K.) with Kinetic and Spectra mode.

Femtosecond transient absorption spectra were recorded on a system based on a Ti:sapphire laser oscillator (Spectra Physics Tsunami) and regenerative amplifier system (BMI Alpha 1000) which produced 100 fs pulses at 800 nm with an average 450–500 mW output power. Excitation pulses at 500 and 540 nm have been obtained by pumping a homemade noncollinear optical parametric amplifier (NOPA) by a portion of the fundamental 800 nm. At all excitation wavelengths the pump beam polarization has been set to magic angle with respect to the probe beam by rotating a $\lambda/2$ plate so as to exclude rotational contributions to the transient signal. Excitation powers were on the order of 30–50 nJ. The probe pulses were generated by focusing a small portion of the 800 nm radiation on a 2-mm-thick sapphire window. After passing through the sample, the white light probe was sent to a flat-field monochromator coupled to a homemade CCD detector. Transient spectra were acquired in a time interval spanning up to 1.5 ns. Measurements were carried out in a quartz cell (2 mm thick) mounted on a movable stage to refresh the solution and avoid sample photodegradation. Transient data were analyzed by global analysis using the software GLOTARAN.²⁹

3. RESULTS AND DISCUSSION

3.1. Molecular Design and Synthesis. A few previously reported orthogonal Bodipy dimers were selected, in order to confirm the putative photoinduced symmetry-breaking intramolecular charge transfer and the following recombination enhanced intersystem crossing ([Scheme 1](#)).^{14,16,30} The selected dimers present several structural differences, which allowed us to explore the relationship between the system structures and their ISC quantum yields. For instance, **BB-1** does not contain

Scheme 1. Structure of the Synthesized Bodipy Dimers **BB-1**, **BB-2**, **BB-3**, **BB-4**, **BB-5**, and **BB-6** and the Reference Compound **1a**



any distinct electron withdrawing or electron donating moieties, whereas **BB-3** has an electron withdrawing 4-nitrophenyl group and **BB-4** an electron donating moiety (4-aminophenyl group). Moreover, **BB-5** and **BB-6** were designed in such a way that their two Bodipy moieties were linked by a benzene ring, not resulting in an orthogonal geometry. Finally, **BB-2**, with a carbazole moiety attached to one Bodipy core, was designed to modify the absorption features of the dimer. However, it had already been proved that although **BB-2** presented a red-shifted absorption band respect to the other systems, it had inefficient ISC compared to **BB-1**,¹⁴ similarly to other π -extended conjugated bis-Bodipy derivatives.^{19,31} Nevertheless, **BB-2** was also prepared to investigate the mechanism of inefficient ISC.

3.2. Single-Crystal Molecular Structures. The molecular structure of a dimeric Bodipy similar to **BB-1** was determined by single-crystal X-ray diffraction.¹² The dihedral angle between the two Bodipy moieties was found to be very close to 90° . In this work, the molecular structures of the Bodipy dimers were investigated by DFT calculations ([Figure 1](#) and [Figure S22](#)).

Moreover, we conducted single-crystal X-ray diffraction measurements also for **BB-3** and **BB-5** to confirm the geometries of the two Bodipy moieties. For **BB-3**, the dihedral angle of C1–C2–C3–C4 is 107.51° ([Figure 1a,c](#)), with a little deviation from an orthogonal geometry. However, the optimized molecular structure determined by DFT calculations displays a strict orthogonal geometry, with a dihedral angle of C1–C2–C3–C4 equal to 90° ([Figure 1d](#)). In the case of **BB-5**, the relative geometry of the Bodipy moieties can be qualitatively inferred by a side view of the compound. The two Bodipy in this case are almost parallel to each other, with a small angle of 2° ([Figure 1b,e](#)), lying on two planes situated at small angle (20° , [Figure 1f](#)) in the optimized geometry. The deviation of XRD results from DFT calculations was supposed not affecting the assignment of the geometries of either **BB-3** or **BB-5**, which from the inference of Akkaya's group that a 30° deviations from orthogonality or planarity maintained excited-state characteristics in CASSCF calculations.¹³

3.3. Steady-State Absorption and Emission Spectra. The steady-state UV–vis absorption spectra and the emission spectra of the synthesized compounds were recorded in solvents with different polarities. In all solvents, the absorption bands of the dimers are similar to the absorption of the Bodipy monomer **1a** ([Figure 2a](#), [Supporting Information](#), [Figure S7](#) and [Figure S8](#)), indicating that the interaction of the two

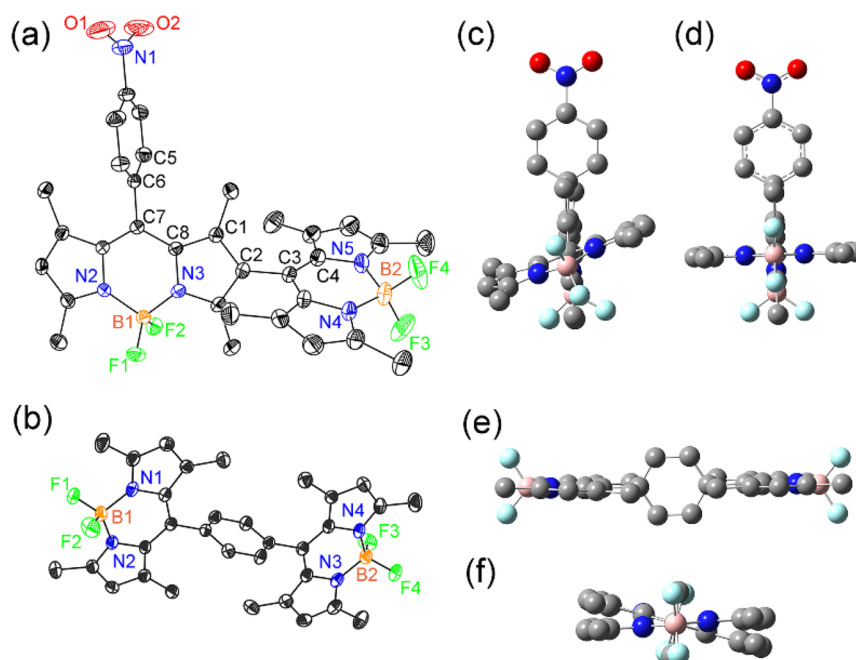


Figure 1. Structures of BB-3 and BB-5. ORTEP diagram (30% probability level) for the X-ray diffraction structure of (a) BB-3, (b) BB-5. Side view for the X-ray diffraction structure of (c) BB-3, (e) BB-5 in ball and stick display style. Optimized geometry of (d) BB-3, (f) BB-5 at the DFT//B3LYP/6-31g(d) level with Gaussian 09W, in combination with a polarizable continuum model (PCM) using dichloromethane as solvent. Hydrogen atoms are omitted for clarity.

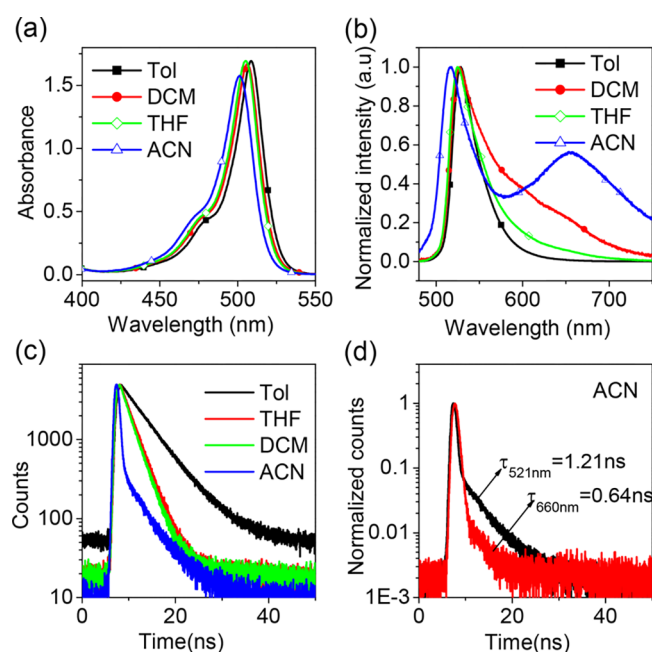


Figure 2. (a) UV-vis and (b) normalized fluorescence spectra of BB-1 ($\lambda_{\text{ex}} = 470$ nm) in different solvents. (c) Fluorescence lifetime of BB-1 in different solvents. Emission was monitored at the peak maximum for each solvent (see Table 1). (d) Fluorescence lifetime of the two emission bands in acetonitrile. Excitation wavelength was 445 nm. c (BB-1) = 1.0×10^{-5} M, 20 °C.

Bodipy moieties in the dimer is weak at the ground state. This result differs from what was observed in the case of chromophore dimers showing an exciton coupling effect, where the absorption splits in two components respect to the spectral signature of the monomer.¹¹

In contrast to UV-vis absorption spectra, the fluorescence emissions of the Bodipy dimers are solvent polarity-dependent (Figure 2b). The fluorescence quantum yields significantly decrease with increasing solvent polarity (Table 1). Moreover, in highly polar solvents, such as acetonitrile, two emission bands are observed, one similar to the emission of a Bodipy monomer and the other occurring in a red-shifted position and assigned to the charge transfer emissive state.^{27,28} The decay time of the latter is less than 1 ns. Furthermore, the maximum of the long wavelength emission band blue-shifts upon lowering the temperature to 77 K, which further confirms its assignment as a charge separation feature (Figure 2 and Figure S14). No red-shifted emission is present in case of BB-5 and BB-6 (Figure S8). For BB-2, upon excitation of the absorption band corresponding to the Bodipy moiety, two fluorescence bands are observed. One is a minor peak at about 520 nm, attributed to the Bodipy monomer emission, while the other, which is red-shifted with increasing solvent polarity, is assigned to the Bodipy–Carbazole intramolecular charge transfer state (Supporting Information, Figure S9). The fluorescence quantum yields are low in both nonpolar and polar solvents. The photophysical parameters of all the analyzed Bodipy dimers are summarized in Table 1 and Table S2.

3.4. Nanosecond Transient Absorption Spectroscopy (ns TAS): The Triplet-State Quantum Yields and Triplet-State Lifetime. Although orthogonal Bodipy dimers had been previously prepared and characterized, the solvent-dependency of their triplet excited state yield and lifetime had not been thoroughly studied by nanosecond transient absorption spectroscopy (ns TAS).^{12,14} Zhang et al. prepared an orthogonal Bodipy dimer containing two chlorine atoms in one Bodipy unit, and the dimer only showed triplet-state production in nonpolar solvents.¹⁵ Here we studied the ns TA spectra of the Bodipy dimers in solvents with different polarity. In all the four selected solvents (toluene, dichloromethane, tetrahydrofuran,

Table 1. Photophysical Parameters of the Bodipy Dimers BB-1, BB-3, and BB-4

	solvent ($E_T(30)$)	$\lambda_{\text{abs}}/\text{nm}$	ϵ ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}$	τ_F/ns	$\Phi_F^a/\%$	$\tau_T/\mu\text{s}$	$\Phi_{\Delta}/\Phi_{\Delta}^b$
BB-1	Toluene (33.0)	509	16.9	528	5.30	80.4	232.1	0.16
	THF (37.4)	505	16.9	525	2.60	6.3	21.3	0.85
	DCM (40.7)	506	16.7	527	2.42	^c	99.3	1.41
	ACN (45.6)	501	15.8	521	0.06 (65%), 0.70 (12%), 4.90 (23%) 0.48 (97%), 5.70 (3%)	0.1	86.1	0.41
BB-3	Toluene	513	14.3	545	4.52	3.3	105.6	0.55
	THF	510	14.9	545	0.06 (45%), 0.7 (44%), 4.63 (11%) 0.39 (92%), 4.70 (8%)	0.1	136.1	^d
	DCM	511	14.4	536	0.05 (50%), 1.65 (21%), 5.91 (29%) 0.76 (91%), 5.89 (9%)	^c	133.9	0.25
	ACN	506	13.9	532	0.02(66%), 0.57(11%), 5.32(23%) 0.26(94%), 5.00(6%)	0.1	135.4	^d
				640				
				660				
BB-4	Toluene	510	7.9	526	4.66	62.8	266.6	0.18
	THF	507	7.7	524/660	0.09(55%), 4.16(45%)	0.1	248.7	^d
	DCM	508	7.6	525	2.75	^c	135.7	0.85
	ACN	504	7.2	519	0.08(60%), 2.17(12%), 5.66(27%) 0.31(95%), 5.17(5%)	0.1	206.1	0.14

^aFluorescence quantum yields (Φ) of BB-1 were calculated using 1,3,5,7-tetramethyl-8-phenyl-Bodipy ($\Phi = 0.72$ in THF) as the standard. ^bRelative to the $^1\text{O}_2$ quantum yield of Rose Bengal ($\Phi_{\Delta f} = 0.80$ in MeOH). ^cNot determined. ^dToo low to be determined accurately.

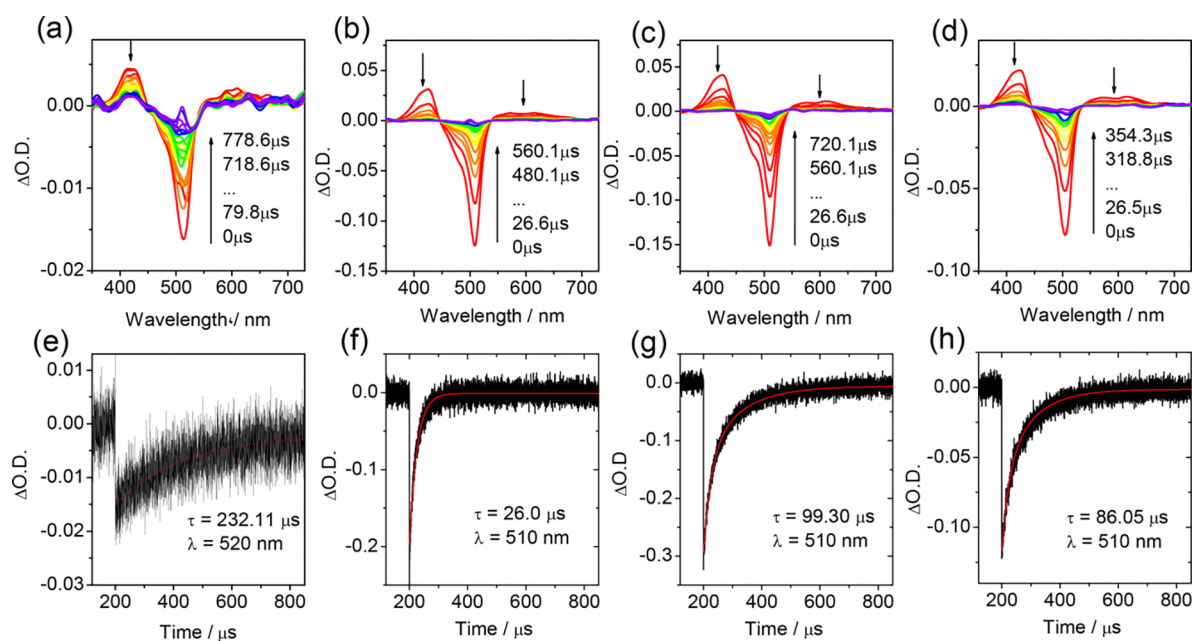


Figure 3. Nanosecond time-resolved transient difference absorption spectra of BB-1 in different solvents. Transient absorption in (a) toluene, (b) tetrahydrofuran, (c) dichloromethane, and (d) acetonitrile. Decay traces at 510 nm ($\lambda_{\text{ex}} = 532 \text{ nm}$) in (e) toluene, (f) tetrahydrofuran, (g) dichloromethane, (h) acetonitrile. c (BB-1) = $1.0 \times 10^{-5} \text{ M}$, 20°C .

and acetonitrile), the TA features of the dimers are similar, since they all correspond to the difference absorption spectrum of the triplet excited state of the Bodipy chromophore. The ns TAS spectra of BB-1 in different solvents are reported in Figure 3, while those of the remaining compounds can be found in Supporting Information.

Triplet-state lifetimes of the Bodipy dimers were obtained by fitting decay of the transient trace at 510 nm. The triplet-state lifetimes determined with the transient absorption spectra are different from the phosphorescence lifetimes of the singlet oxygen obtained by Ortiz and coworkers.¹⁶ Given that the triplet-state lifetime of the compound is long ($> \text{ca. } 1 \mu\text{s}$), the singlet oxygen quantum yield is directly related to the triplet-state quantum yield of the compounds, because the singlet oxygen is

produced via the triplet–triplet-energy-transfer (TTET) between the triplet photosensitizers and the triplet acceptor. The optical density (OD) value of ns TAS spectra is directly related to the triplet-state quantum yields, making it possible to use the OD values of the bleaching band to evaluate the triplet-state quantum yields of the Bodipy dimer in different solvents. For BB-1, the OD values are larger in solvents with moderate polarity (dichloromethane and THF), than in a nonpolar solvent (toluene) or a highly polar solvent (acetonitrile, Figure 3). This result is in agreement with the recent report on the singlet oxygen quantum yields (Φ_{Δ}) of Bodipy dimers in different solvents.¹⁶ Similar results were observed for BB-4, although the intensity of the bleaching signals are in this case smaller than those of BB-1, indicating lower triplet quantum

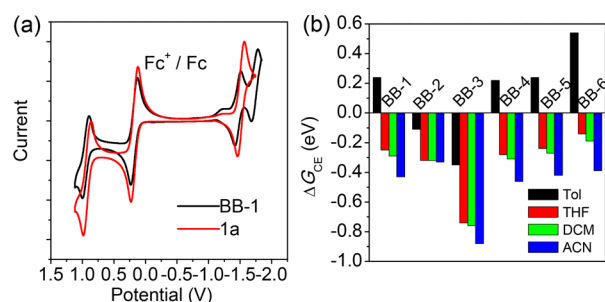


Figure 4. (a) Cyclic voltammogram of BB-1 and reference compound 1a. Ferrocene (Fc) was used as the internal reference [$E_{1/2} = +0.06$ V (Fc⁺/Fc) vs standard hydrogen electrode]. In deaerated CH₃CN solutions containing 0.10 M Bu₄NPF₆ as supporting electrolyte and with Ag/AgNO₃ reference electrode. Scan rates: 50 mV/s. 20 °C. (b) Calculated free energy changes of the charge separation (ΔG_{CS}) in different solvents.

yields for this compound (Supporting Information, Figure S12). In the case of BB-3, the triplet quantum yield in toluene is the highest; it decreases slightly in DCM and THF and further in acetonitrile (Supporting Information, Figure S11). The properties of BB-3 are thus different from those of BB-1 and BB-4, which is mainly due to the presence of the electron withdrawing 4-nitrophenyl group. By comparing the intensity of the bleaching signals and the singlet oxygen quantum yields, it was found that the presence of both an electron withdrawing and an electron donating group reduces the triplet quantum yields of these Bodipy dimers. Ortiz and co-workers had presented an explanation for such substitution patterns based on quantum chemical calculations, which drawn an opposite conclusion.¹⁶ No long-living triplet state could be detected for BB-2, BB-5, and BB-6, indicating weak ISC or short triplet-state lifetime.

3.5. Electrochemical Measurements. Initially, a “doubly substituted” excited state was proposed to be responsible for the ISC of the orthogonal Bodipy dimers.^{12,13} Recently, more evidence was presented to support an intramolecular charge transfer (or electron transfer) mechanism.^{16,17} However, no solid evidence was reported for the charge transfer mechanism. Concerning this aspect, a calculation of the Gibbs free energy changes (ΔG_{CS}) for the putative photoinduced electron transfer process and the energy level of the CSS (E_{CSS}), as well as the comparison of the latter with the S₁ state and the T₁ state energy levels, will be helpful for validation of the ISC mechanism.

The cyclic voltammogram of BB-1 is reported in Figure 4. A reversible oxidation wave, similar to that of a Bodipy monomer, was observed as +0.95 V. Two reversible reduction waves were recorded at −1.47 V and −1.73 V, respectively. For the

monomer 1a, however, only one reversible reduction wave was observed, at −1.51 V (Table 2).

Similar results are found for other Bodipy dimers with the exception of BB-3 (Figure S13), where the first reduction peak is distinctly different by shape and intensity from 1a and other dimers. The first reduction potential is anodically shifted by about 0.25 V upon addition of the electron withdrawing 4-nitrophenyl group; thus, the difference between the first oxidation and reduction potentials (electrochemical gap, ΔE_{redox}) is significantly reduced with respect to BB-1. The E_{CSS} of BB-3 in toluene is +2.23 eV, and ΔG_{CS} is −0.15 eV, indicating that the formation of the T₁ state through CR in toluene is thermodynamically allowed. However, the driving force for the formation of the T₁ state decreases with increasing solvent polarity, which rationalizes the decrease of the singlet oxygen quantum yields in polar solvents. This result is in agreement with that from ns TAS and similar results had been observed on a Bodipy dimer containing a 4-dichlorobenzene group.¹⁵

For Bodipy dimers BB-5 and BB-6, however, no ISC was observed, although the photoinduced charge transfer is thermodynamically allowed in both molecules (Figure 4b), and it is confirmed by the fs TAS studies (see later sections). It is noticeable that for BB-2 the first oxidation potential is cathodically shifted by about 0.19 V, and the first reduction potential is anodically shifted by about 80 mV as compared to those of compound 1a. Therefore, it can be concluded that the presence of the electron-donating carbazole moiety facilitates the charge separation. Furthermore, the occurrence of charge transfer between the carbazole and the Bodipy moieties has been confirmed through fs TAS measurements (see later sections).

3.6. Femtosecond TAS Spectroscopy. Charge Separation (CS) and Charge Recombination (CR) Processes: Origin of the ISC. Despite the formation of a red-shifted short-lived emission band and the observation that charge transfer in polar solvents is thermodynamically allowed, further evidence for the occurrence of CS and CR processes in Bodipy dimers, which were assumed to be at the origin of ISC, was rarely investigated. Herein, we measured femtosecond transient absorption spectra (fs TAS) in different solvents to confirm the presence of CSS and to study the dynamics of such processes.

The recorded TAS spectra were analyzed with a global analysis procedure using a sequential decay scheme.³² The EADS (Evolution Associated Decay Spectra) obtained from global analysis show that the excited state evolution of BB-1 depends on the solvent polarity (Figure 5), as it is also evident by comparison of the kinetic traces registered around 500 nm (Figure 6). In the more polar solvents DCM (Figure 5c) and acetonitrile (Figure 5d), the initial spectral component is

Table 2. Electrochemical and Optical Properties of Compounds 1a and Bodipy Dimers

	$E^{1/2}_{(OX)}$ (V)	$E^{1/2}_{(RED1)}$ (V)	$E^{1/2}_{(RED2)}$ (V)	E_{redox} (V)	$E_{0,0}$ (eV)	E_T (eV)
1a	+0.92	−1.51		2.44	2.44	
BB-1	+0.95	−1.47	−1.73	2.41	2.41	1.68, ^a 1.50 ^b
BB-2	+0.73	−1.39	−1.68	2.12	2.12	1.82 ^b
BB-3	+0.96	−1.22	−1.72	2.18	2.38	1.67, ^a 1.50 ^b
BB-4	+0.92	−1.47	−1.73	2.39	2.40	1.51 ^b
BB-5	+0.99	−1.44		2.43	2.43	2.00 ^b
BB-6	+1.00	−1.42	−1.54	2.42	2.40	1.98 ^b

^aDetermined by low temperature photoluminescence spectra at 77 K. ^bDFT calculation.

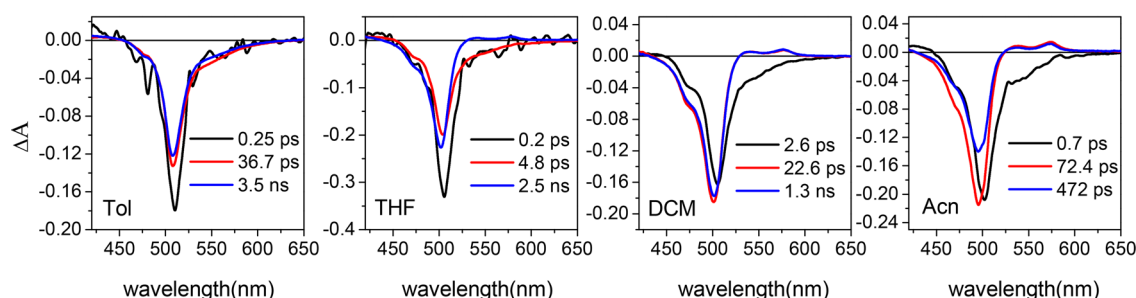


Figure 5. EADS obtained from global analysis of transient absorption data recorded for sample BB-1 in the analyzed solvents: (a) toluene, (b) tetrahydrofuran, (c) dichloromethane, (d) acetonitrile. All the samples were excited at 490 nm, using excitation powers of about 30 nJ.

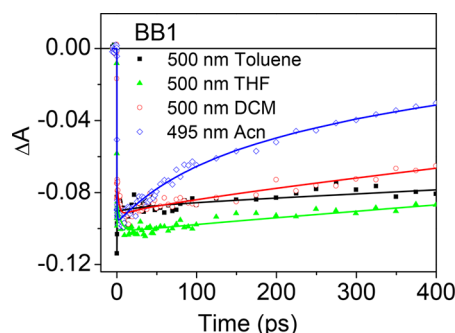


Figure 6. Kinetic traces registered at the maximum of the bleaching signal for BB-1 in different solvents.

characterized by the appearance of a negative band, corresponding to the convolution of ground-state bleaching (GB) and stimulated emission (SE) (Figure 2), broadened at the red part of the spectrum. On a picosecond time scale (0.7 ps in the case of ACN and 2.6 ps for DCM), two positive bands are distinguishable at about 535 and 575 nm. At the same time, the maximum of the negative peak apparently shifts toward shorter wavelengths. This evolution can be associated with the formation of CSS in the system, while the two positive bands can be attributed to the absorption of Bodipy cation ($\text{BDP}^{+\bullet}$) and anion ($\text{BDP}^{-\bullet}$) species, respectively.^{27,33–35}

Table 3. Kinetic Rates for Possible Processes of BB-2 in Different Solvents Determined by Global Analysis Fitting of Femtosecond TAS Measurements

BB-2	Solvent	$1/(k_{\text{IC}}+k_{\text{CS}})$ (ps)	$1/k_{\text{rec}}(\text{ns})$
$\lambda_{\text{ex}} = 495 \text{ nm}$	Tol	2.3	1.10
	THF	2.5	0.41
	DCM	2.0	0.44
	ACN	0.9	0.07
$\lambda_{\text{ex}} = 540 \text{ nm}$	Tol	1.3	1.10
	THF	0.8	0.34
	DCM	0.6	0.37
	ACN	0.7	0.07

In toluene (Figure 5a), no positive bands developed, implying that CS is either not active or it has very low QY in this nonpolar medium, in agreement with the electrochemical analysis. Moreover, the GB band is narrower than in other solvents, and much more similar to the feature observed for an isolated Bodipy 1a (Supporting Information, Figure S15). The signal shows a fast initial decay, which can be associated with the evolution from the instantaneously reached Franck–Condon (FC) state toward a local excited (LE) state, followed by a biexponential decay on a 36.7 ps and 3.5 ns time scales. In acetonitrile, the signal intensity significantly decreases on a 72.4 ps time scale, until the complete recovery of the ground state within 472 ps. In DCM, the signal disappearance occurs on a

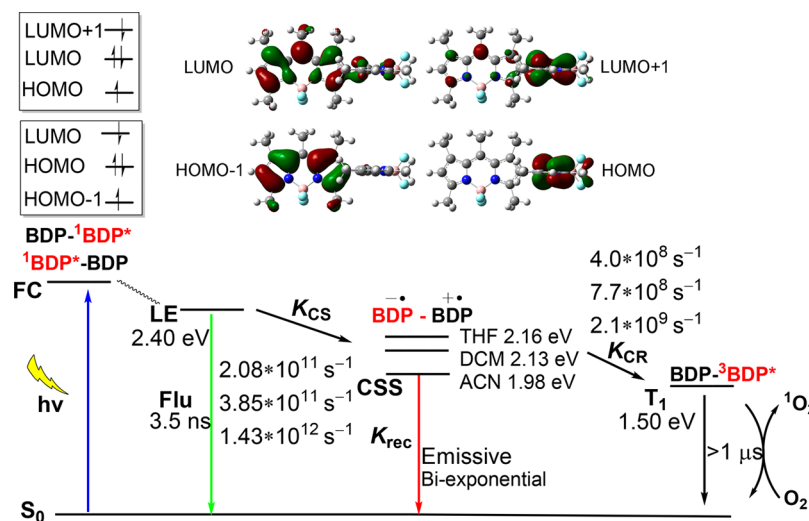


Figure 7. Illustrative diagram of the electronic state energy levels and excited states kinetics involved in Bodipy dimer BB-1. K_{rec} is the total rate for recombination to either the triplet or ground state. The excitation energy and involved frontier orbitals were calculated at the optimized ground-state geometries. TD-DFT calculations were performed at the B3LYP/6-31G(d) level with the Gaussian 09W package.

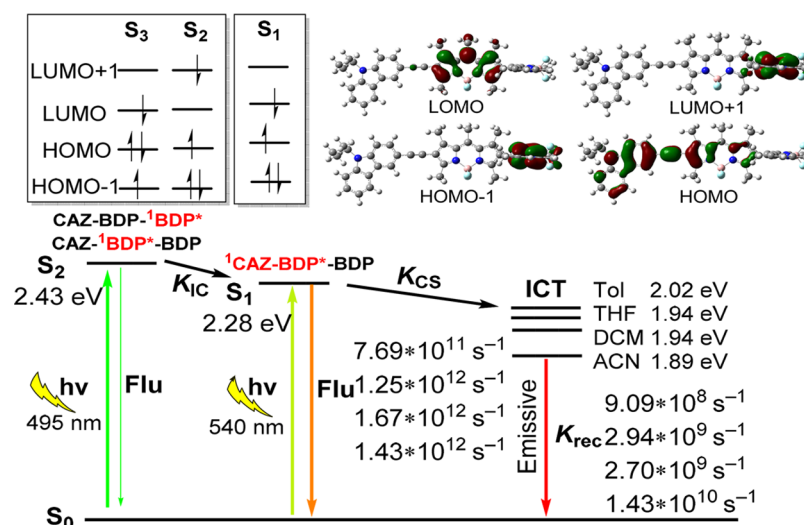


Figure 8. Illustrative diagram of the electronic state energy levels and excited states kinetics involved in the singlet oxygen production from Bodipy dimer BB-2. K_{IC} is the rate of internal conversion. Excitation energy and involved frontier orbitals were calculated at the optimized ground-state geometries. Calculation was performed at the B3LYP/6-31G(d) level with Gaussian 09W TD-DFT calculations.

slower time scale of 22.6 ps and 1.3 ns. Since the triplet transient species absorbance is very similar to that of the CS species (Figure 3), we could not observe any new absorption signal representing charge recombination to produce the triplet excited state. However, the degree of singlet oxygen photosensitization in different solvents could be associated with the degree of signal recovery. Thus, the significant signal decay on a 72.4 ps time scale in acetonitrile verify that the ISC will not be efficient in polar solvents as it is in dichloromethane.

The evolution of the transient signal in THF is different: here we observed an initial very fast decay of the negative bleaching signal, occurring on a sub-picosecond time scale. Then, on a 4.8 ps time scale, very weak positive bands appear in the red region of the spectrum, and at the same time the negative band slightly increases in intensity and blue shifts. This evolution is also attributed to the formation of CSS. The yield of charge separation appears lower than in DCM and ACN, considering the intensity of the positive bands. Furthermore, the signal disappears on a longer time scale than in more polar media, further demonstrating that the yield of charge separation is minor. Overall, a simplified Jablonski diagram is proposed to explain the obtained results (Figure 7).

Similar results were observed for BB-4 (Supporting Information, Figure S17). In this case, positive features indicating the occurrence of CS are also observed in ACN, DCM, and THF. The charge separation state is formed within 0.45 ps in ACN, 1.7 ps in DCM, and 1.3 ps in THF. The amount of CS appears particularly high in THF, where the intensity of the positive bands is higher than in the other two solvents. However, the overall lifetime of the excited state is quite short in this solvent (176 ps in THF), even shorter than that observed in the more polar acetonitrile (440 ps in ACN and 1.3 ns in DCM). Though the yield of CS is high in THF, the fast CR and GS recovery imply inefficient ISC of BB-4 in THF, which is consistent with the lowest singlet oxygen photosensitization quantum yield (Table 2). In toluene there is no evidence for the formation of a CS state, in agreement with what observed in fluorescence emission studies (Figure S8).

The evolution of the excited states in BB-3 is also solvent dependent (Figure S16). For this molecule, however, the amount of CS appears always to be lower than in case of BB-1.

Only in acetonitrile can we clearly distinguish two positive peaks attributable to anion and cation species. In both THF and DCM a broad, low-intensity positive band extending between 530 and 600 nm develops. The time scale associated with the appearance of CS is within 2 ps, faster in acetonitrile (0.5 ps), and slightly slower in DCM (0.8 ps) or THF (1.6 ps). The overall lifetime of the excited state is highly dependent on the solvent properties, as can be observed by comparing the kinetic traces (Supporting Information, Figure S16) registered at the maximum of the bleaching signal. For this molecule, a broad positive band is also observed in toluene, indicating that in this case CS is also possible in the nonpolar solvent, which is consistent with the electrochemical results. In acetonitrile and THF (Supporting Information, Figure S16d and S16b), the CS signal intensity significantly decreases and the ground state is completely recovered on a 284 and 555 ps time scale, respectively, which could explain the inefficient 1O_2 photosensitization of BB-3 in these two solvents (Table S1). Moreover, although the intensity of the positive CS signals is similar in toluene and DCM, the slower recovery time (3.7 ns in toluene and 696 ps in DCM) indicates that in toluene ISC is more efficient.

When considering the apparently very similar compounds BB-5 and BB-6, the evolution of their excited-state signals upon photoexcitation appears to be different in polar solvents (Supporting Information, Figure S18). In fact, the excited state evolution of BB-5 is almost independent of the solvent polarity. For this dimer, the transient spectra in all solvents remind those of an isolated Bodipy moiety, except for a slight broadening of the negative band. This result suggests that the excited state is delocalized on both chromophores, in agreement with the computational results (Supporting Information Figure S22). The transient spectra can be fitted with three kinetic components. In each case, a very fast decay component (0.5–0.7 ps) can be observed, representing a relaxation of the excited state due to an electron density redistribution between the two chromophores of the dyads. No CS absorption bands are observed in THF and toluene, so that the intermediate component (10–12 ps) could be assigned to vibrational cooling. This contribution is significantly longer in DCM, where it is mostly associated with a decay of the red-

most part of the signal (see the red to blue evolution in Figure S18c), possibly indicating the occurrence of CS in this solvent, however, the induced absorption around 535 nm is obscured by the overlap with the stimulated emission band. **BB-5** is not very soluble in acetonitrile, but the presence of a CS process cannot be excluded in this solvent, since the fluorescence quantum yield and the fluorescence lifetime are lower/shorter in polar solvents. Moreover, in a previous report from Whited et al., fs TAS was also conducted for a similar compound in toluene and acetonitrile.²⁶ A small ICT state absorption of Bodipy radical anion and cation was observed in acetonitrile. They also claimed that CS is much more efficient in the second compound which they studied, very similar to our **BB-1**. Consistently with their findings we observe that CS is efficient in case of **BB-1**. In all cases the recovery of GS is almost complete on a time scale of about 2 ns.

In the case of **BB-6**, the excited state evolution is much more dependent on the solvent polarity. In all solvents the first spectral component (black line in the EADS of **BB-6**) is much broader than the corresponding feature measured for **BB-5**, suggesting that the excited state is more delocalized over the two monomers (Supporting Information, Figure S22). After a fast electron density redistribution, a pronounced, broad positive CS absorption band appears on the time scale of 29 and 57 ps in acetonitrile and DCM, respectively. In THF, no positive feature is observed, while the negative band is quite broadened on the red side and decays on a nanosecond time scale without any significant spectral evolution. The GS recovery occurs on a nanosecond time scale in all solvents except acetonitrile, where a very fast recombination process is observed (83 ps).

Symmetry-breaking intramolecular charge transfer (SBCT) is supposed to be the operative mechanism accounting for charge separation in the excited state of these Bodipy dimers (**BB-1**, **BB-3**, **BB-4**, **BB-5**, and **BB-6**).^{26–28} The particularly strong coupling between the two units in **BB-5** and **BB-6** is responsible for the lack of distinctive CS features and the disappearance of the red-shifted emission in polar solvents, since a much stronger symmetry breaking would be needed to induce an appreciable dipole moment in these systems.²⁸ The lack of ISC for dimers **BB-5** and **BB-6** is due to the geometry of the two Bodipy moieties, which are not linked perpendicularly but lie in a nearly planar configuration (Figure 1). In this situation, CR does not induce any variation of the molecular orbital angular momentum, so that the conditions for the occurrence of SOCT-ISC are not satisfied.²⁰

Although bis-Bodipy derivatives with extended conjugation had already been proved inefficient for photosensitization by quantum mechanical simulation and experiments,^{13,14,31} we identified a new mechanism accounting for the inefficient emission and ISC processes in **BB-2**.

Carbazole is a well-known electron donor moiety, so that following excitation, a species with intramolecular charge separation (ICT state) may become the lowest energy state in polar solvents.¹ In fact, the fluorescence spectra in different solvents (Supporting Information, Figure S9) and electrochemical analysis of **BB-2** had proved the presence of another emissive state, most probably the ICT state. Femtosecond TAS has been conducted with excitation at 495 and 540 nm for individually activating the two fluorophores of **BB-2** in the four solvents mentioned above. Two or three kinetic components were sufficient in order to correctly fit the data.

Excitation at 495 nm is mainly localized on the Bodipy moiety, but non-negligible contributions due to a GB band and a SE band of the Bodipy-Carbazole unit, peaking at about 540 nm and expanding up to 750 nm, are present. The negative feature, at *ca* 505–510 nm, corresponds to GB of the Bodipy chromophore (Supporting Information, Figure S20). Fast internal conversion (IC) could contribute to the ultrafast excited-state energy redistribution, as TD-DFT calculations show that the initially excited state is either S_2 or S_3 , which are dark states according to their computed Oscillator Strengths (f) (Supporting Information, Table S6). However, the kinetics of this process could not be distinguished in our experiments. Then we observed an intensity decrease of the Bodipy-Carbazole unit GB and the first SE band at a time scale of 0.9 ps in ACN, 2.0 ps in DCM, 2.5 ps in THF, and 2.3 ps in toluene, respectively. At the same time, a red-shifted new SE band peaking at 700 nm in ACN, 650 nm in DCM and THF, and 610 nm in toluene develops, which could be assigned to the emission of the ICT state. This spectral evolution occurs on a longer time scale respect to what happens when the system is excited at 540 nm (Table 3). In this case, no internal conversion is observed, suggesting that this process becomes significantly faster due to the occurrence of CS. In THF the 54 ps component does not lead to any significant spectral evolution, but its inclusion in the fitting of the kinetic traces significantly improves the result. Although excitation at 540 nm is mostly concentrated on Bodipy-Carbazole moiety, Bodipy moiety GB is always present (Supporting Information, Figure S20). As mentioned above, the CS process is faster upon direct excitation of the Bodipy-carbazole unit in all solvents. In order to graphically summarize all the obtained results, a simplified Jablonski diagram is sketched in Figure 8.

CONCLUSION

In this work, we present the first direct evidence that photoinduced charge separation followed by charge recombination leads to the occurrence of ISC in orthogonal Bodipy dimers. Three kinds of Bodipy dimers, containing orthogonally or nonorthogonally linked Bodipy units, or with π -extended conjugation linkers, were prepared. The photophysical properties of all systems were investigated with steady-state and time-resolved transient spectroscopies. The occurrence of photoinduced charge transfer between Bodipy moieties in symmetric Bodipy dyads was confirmed by the presence of a red-shifted charge transfer emission band (*cs.* 660 nm in acetonitrile for **BB-1**, **BB-3**, and **BB-4**). In the case of **BB-2**, the observed red-shifted emission band (*cs.* 640 nm in THF and DCM, 657 nm in acetonitrile) is attributed to the formation of an intramolecular charge transfer state of the Bodipy-Carbazole moiety. Despite no such band being found for **BB-5** and **BB-6** in the steady-state emission spectrum, we observed the occurrence of charge separation in polar solvents through femtosecond transient absorption spectroscopy. In this case, the occurring of symmetry-breaking intramolecular charge transfer (SBCT) was proved by the appearance of $BDP^{+\bullet}$ and $BDP^{\bullet-}$ absorption bands at 535 and 575 nm in the transient spectra. Although charge separation was observed for all the species, we found that only in the case of **BB-1**, **BB-3**, and **BB-4**, the following charge recombination process is able to induce the formation of a triplet state. We also found that the triplet quantum yield is dependent on the solvent polarity, and that ISC is more efficient in solvents with moderate polarity. These observations are supported by TD-DFT calculations, showing that the

energy level of the charge separated state is high in nonpolar solvents and low in polar solvents, implying that a CR-induced ISC has the largest driving force in solvents with moderate polarity. The complete photochemical characterization of the analyzed systems performed in this study clarified the mechanism of the SOCT-ISC in orthogonal symmetric Bodipy dimers. This information will be useful for further studies of the fundamental photochemistry of organic chromophores, and to develop new strategies to achieve ISC in heavy atom-free organic chromophores.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b10213.

Experimental procedures, molecular structure characterization, nanosecond transient absorption and femtosecond transient absorption experimental details, electrochemical experiment and additional spectra, and crystallographic data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: klhan@dicp.ac.cn.

*E-mail: zhaojzh@dlut.edu.cn.

*E-mail: didonato@lens.unifi.it.

ORCID

Jianzhang Zhao: 0000-0002-5405-6398

Mariangela Di Donato: 0000-0002-6596-7031

Ke-Li Han: 0000-0001-9239-1827

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the NSFC (21473020, 21673031, 21273028, 21421005, 21761142005, and 21603021), the Fundamental Research Funds for the Central Universities (DUT16TD25, DUT15ZD224, DUT2016TB12) for financial support.

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