DOI: 10.1002/ejoc.201200958



Metal-Free Benzodithiophene-Containing Organic Dyes for Dye-Sensitized Solar Cells

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Keywords: Donor-acceptor systems / Dyes/pigments / Sensitizers / Solid state structures / Solar cells

Two new metal-free organic dyes, **CR29** and **CR52**, with high extinction coefficients in the visible spectral region between 400–650 nm, have been synthesized. The donor–acceptor structure of the dyes feature benzodithiophene moieties **BDT₁** and **BDT** as rigid π -conjugated spacers, which have so far been very little studied for dye-sensitized solar cell (DSSC) applications. DFT/TDDFT calculations have been employed to guide the design of the chromophores as well

Introduction

Dye-sensitized solar cells (DSSC or Grätzel cells) are photovoltaic devices that are the object of competitive and extensive research aimed at improving efficiencies and reducing costs.^[1] One of the key components in a DSSC is the dye, which is responsible for harvesting the sunlight and injecting electrons into the mesoporous semiconducting oxide, typically TiO₂.

Metal-based photosensitizers have been used over the last 20 years as the key components for DSSCs.^[1e,2] So far, record efficiencies of 12.3% under AM 1.5 conditions have been reached by using Zn^{II} porphyrin dyes and cobalt poly-

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200958.

as to shed light on their electronic and optical properties. Photophysical and electrochemical characterization studies have been carried out to gather information on the charge transfer processes occurring at the dye–semiconductor interfaces. Under standard AM 1.5 conditions, DSSC sensitized with **CR29** showed good conversion efficiencies: 5.14 % in the liquid electrolyte cell setup and 2.47 % in the solid-state DSSC.

pyridyl redox electrolyte.^[3] Although transition metal dyes exhibit high performances, challenging synthesis and complex purification steps are often required. For these reasons, in recent years, alternative metal-free organic dyes have attracted great attention. In fact, such chromophores can be prepared rather inexpensively by using well-established synthetic methodologies and they present optical, electronic, and electrochemical properties that can be modulated through appropriate molecular design.^[4]

The development of innovative, stable organic dyes with optical absorptions extending into red and near-IR regions of the solar spectrum is, at present, a "hot topic" of research in this field. The most efficient metal-free organic dyes are characterized by a donor- π -acceptor (D- π -A) structure, in which the donor group (D) is an electron-rich unit, linked through a conjugated π -bridge spacer to the electron-acceptor group (A). In the cell, unit A is bound to the semiconductor surface (TiO₂), usually through a carboxylic or cyanoacrylic acid function. The nature of the conjugated bridging segment (π) has proved to be of significant importance for controlling the light-harvesting performance of the dye and a number of new π -conjugated aromatic and heteroaromatic systems^[4] have been investigated. Among these, the use of several kinds of substituted thiophene or thienothiophene derivatives as π -bridges, have been reported to give remarkable efficiencies.

Benzo[1,2-*b*:4,3-*b*']dithiophene (**BDT**) and benzo[1,2*b*:4,5-*b*']dithiophene (**BDT**₁; Figure 1) attracted our attention because of their stable, rigid, π -conjugated condensedpolycyclic structures.^[5] These features lead to unique elec-

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tronic properties such as high conductivity, field-effect mobility, and tunable stacking in the solid state; moreover, rigid structures hamper the roto-vibrational modes responsible for the deactivation of the excited states in functional materials.^[5c] In this context, **BDT** and **BDT**₁ therefore look to be important frameworks in functional organic materials for optoelectronic devices.^[6] Although **BDT**₁ has already been incorporated in conducting polymers employed in BHJ solar cells,^[7] to the best of our knowledge, only one recent report utilizes a 3-bromo-4,8-diisopropoxy-**BDT**₁ as the π -conjugated spacer incorporated into a D- π -A DSSC dye.^[8]



Figure 1. Structure and numbering scheme of BDT and BDT₁.

Due to the above considerations, with the aim of establishing a structure/performance correlation of dyes endowed with **BDT** and **BDT**₁, a systematic study of donor-acceptor systems obtained by coupling BDT_1 and BDT with traditional and new A and D groups is ongoing. As part of a more general research program undertaken in our laboratories^[9] in this work we wanted to investigate the ability of **BDT**₁ and **BDT**, acting as π -bridge spacers, to enhance the overall performance of dyes. We report here the synthesis, the optical and electrochemical characterization, and the photovoltaic properties of two novel BDT₁- and BDT-based chromophores, respectively named CR29 and CR52 (Figure 2), along with their DFT/TDDFT computational characterization. In both CR29 and CR52 the donor and the acceptor fragments are constituted by the classical triarylamino and cyanoacrylic groups. The triarylamine moiety is linked to the BDT_1 and BDT spacers through a double bond.



Figure 2. Structures of CR29 and CR52.

Results and Discussion

1.1 Synthesis of the Chromophores

The synthetic strategy envisioned for the preparation of dyes CR29 and CR52 used two isomeric BDT_1 and BDT dialdehyde derivatives 2 and 3 as starting materials (Scheme 1). In fact, by adjusting the reaction stoichiometry, it was possible to selectively react, step by step, the two formyl groups with two different reagents, thus obtaining the target compounds.

In detail, known phosphonium salt $1^{[10]}$ gave aldehyde 4 through Wittig reaction with one of the two carbonyl groups of 2,6-benzo[1,2-*b*:4,5-*b'*]dithiophenedicarbaldehyde (2).^[11] Subsequent Knoevenagel condensation of 4 with cyanoacetic acid, in acetonitrile solution and in the presence of piperidine, led to the target dye **CR29** as a red solid. Similarly, **CR52** was obtained as a red solid, starting from aldehyde 3 and following the same procedure used for **CR29**. The molecular structure of both dyes was confirmed by ¹H and ¹³C NMR, and MS characterization. Reversephase HPLC analysis was employed to establish the purity of those samples submitted to DSSC fabrication; being, in both cases, higher than 98%.



Scheme 1. Synthetic procedures for the synthesis of **CR29** and **CR52**. *Reagents and conditions:* (i) DMF, K_2CO_3 , 18-crown-6, room temp. 15 h. (ii) CNCH₂CO₂H, piperidine, CH₃CN, 80 °C, 4 h.

1.2 Theoretical Calculations

The molecular and electronic structure and the excited state of **CR29** and **CR52** were investigated by performing DFT/TDDFT calculations. The two dyes are characterized by a planar arrangement between the donor N lone pair and the acceptor cyanoacrylic group, which ensures a strong conjugation across the donor- π -bridge assembly. A schematic representation of the HOMO and LUMO of the two dyes obtained by B3LYP/6-31G* calculations^[12,13] is displayed in Figure 3 along with their isodensity plots. Table 1 reports the calculated frontier orbital energies in acetonitrile environment.



Figure 3. Energy diagram and isodensity plots of the HOMO and LUMO of **CR29** (left) and **CR52** (right).

Table 1. Calculated HOMO-LUMO values for CR29 and CR52.^[a]

	НОМО	LUMO	
CR29	-4.73	-2.83	
CR52	-4.70	-2.74	

[a] B3LYP/6-31G* in CH₃CN solution.

Our results show the characteristic HOMO-LUMO pattern of these D- π -A dyes, with the HOMOs essentially confined to the donor moiety and partially spreading over the conjugated π -bridge, whereas the LUMOs extend from the linker to the cyanocrylic acid, with the largest components being localized on the latter. The HOMO localization in the outer molecular region ensures exposure of the oxidized dye, generated after photoinduced electron injection into the TiO₂, to the dye regenerating medium, therefore favoring rapid hole transfer from the oxidized chromophore. The LUMO distribution close to the anchoring group enhances the orbital overlap with the titanium manifold of unoccupied states, assisting the electron injection step. A comparison of the two dyes shows for CR52 a slight destabilization of the LUMO with respect to CR29, due to the reduced conjugation in the former, whereas the HOMO is located at essentially the same energy in the two dyes. Considering the HOMO-LUMO localization, this electronic structure pattern is not surprising, since the two dyes share the same donor moiety and differ in the acceptor; thus, a consequent slight increase of the HOMO-LUMO gap is observed on going from CR29 to CR52. The results of TDDFT excited state calculations performed with the MPW1K functional on the two dyes are reported in Table 2.

Table 2. Computed excitation energies (eV, nm) and oscillator strength (f), using the MPW1K xc functional, for the optical transition of **CR29** and **CR52** dyes, in acetonitrile solution.

CR29					
State	E [eV]	λ [nm]	f	Compositio	n [%]
1	2.56	484	1.73	H→L	79
2	3.50	354	0.81	$H-2 \rightarrow L$	40
				$H \rightarrow L+1$	23
3	3.62	342	0.15	$H-2 \rightarrow L$	19
				$H \rightarrow L+1$	58
CR52					
State	E [eV]	λ [nm]	f	Composition [%]	
1	2.61	476	1.12	H→L	82
2	3.38	367	1.01	$H-1 \rightarrow L$	40
				$H \rightarrow L$	14
				$H \rightarrow L+1$	27
3	3.44	360	0.26	$H-1 \rightarrow L$	36
				$H \rightarrow L+1$	46
4	3.60	344	0.20	$H-4 \rightarrow L$	13
				$H-2 \rightarrow L$	63

For both dyes we calculate a single, low-lying transition with large oscillator strength (f), followed, at higher energy, by a series of additional transitions. For **CR29** and **CR52** we calculate the low-energy excitations at 484 and 476 nm,



Figure 4. Optical absorption spectra of **CR29** (top) and **CR52** (bottom) in different solvents. All spectra are acquired in the presence of TFA.

respectively, which is consistent with the experimental absorption spectrum. These transitions, of HOMO to LUMO character, are the typical charge transfer (CT) excitations of this type of donor-acceptor dyes, leading to charge displacement from the donor to the acceptor dye moiety. The most notable difference between CR29 and CR52 is the considerable decrease of the oscillator strength (1.73 vs. 1.12) for the charge transfer transition that is observed for CR52, along with a slight blue-shifted CT transition (484 vs. 476 nm). This behavior, which is also seen in the experimental absorption spectra (Figure 4), can be related to a 'breakout' of the conjugation, resulting from the different spacer group, across the CR52 donor-acceptor moiety. For both dyes, we assign the transitions in the UV region as originating from π - π * excitations. It is worth noting that TDDFT calculations nicely reproduce the redshift of the π - π^* transitions measured experimentally for CR52 compared with CR29, which are found at ca. 400 nm in the former and at ca. 370 nm in the latter, see Figure 4.

1.3. Optical and Electrochemical Characterization

The molar absorptions of the two dyes in different solvents are reported in Figure 4 (for full absorption profiles, see Figure S7 in the Supporting Information). Compound CR29, possibly due to its linear and planar structure, suffers from aggregation and limited solubility except in tetrahydrofuran (THF) and EtOH solutions. We found the beneficial effect of trifluoroacetic acid (TFA) in dissolving the chromophore,^[14] therefore the molar absorptions have been recorded upon addition of TFA to all the CR29 solutions and, for better comparisons, also to solutions of CR52 (in the solutions, the TFA concentration was ca. $0.5-1 \times 10^{-3}$ M with respect to the $1.2-2.0 \times 10^{-5}$ M dye concentration). Compounds CR29 and CR52 display absorption onsets around 650 nm, and two main transitions in the visible region, as predicted by quantum chemical calculation. In both cases, the high energy transition, peaking around 370-400 nm, shows a poor solvatochromic effect and has been tentatively attributed to a π - π * transition of the conjugated D- π -bridge system. This band is significantly shifted to lower energy in CR52 (ca. 400 nm) compared with CR29 (ca. 375 nm). On the other hand, the low energy transition (around 500 nm) is more sensitive to the solvent polarity and has been assigned to a charge transfer (CT) transition, as already described in the theoretical section. The CT band shifts towards the red, in both dyes, following the order THF, AcCN \approx EtOH, toluene, CH₂Cl₂ (see Table 3; for THF and EtOH spectra see Figure S7 in the Supporting Information).

Corroborating the TDDFT calculations, the **CR29** CT band displays, on average, higher extinction coefficients than **CR52** (respectively being ca. 3.5 and $2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Another interesting aspect that substantially differentiates the two chromophores is the relative intensity of the π - π * and CT bands. The ratio of the two bands is roughly 2:1 in **CR52** and 3:4 in the **CR29** dye. The



Table 3. Experimental optical absorption coefficients of **CR29** and **CR52** in a range of solvents in the presence of TFA.

Solvent	CR29 λ [nm], [ϵ (10 ⁵ cm ⁻¹ M ⁻¹)]	CR52 λ [nm], [ϵ (10 ⁵ cm ⁻¹ M ⁻¹)]
THF	477 [3.71], 373 [2.64]	461 [2.51], 392 [4.16]
AcCN	480 [4.05], 379 [2.86]	464 [2.57], 391 [4.21]
EtOH	480 [3.34], 379 [2.42]	465 [2.27], 394 [3.83]
Toluene	496 [3.15], 379 [2.17]	484 [2.06], 397 [3.81]
CH ₂ Cl ₂	502 [3.48], 380 [2.71]	489 [2.68], 399 [5.52]

higher transition probability of the CT band in **CR29** is a consequence of the better conjugation ability of the linear **BDT**₁ spacer than **BDT**. Indeed, as previously discussed, the CT transition is of HOMO to LUMO character (Figure 3). Whereas the LUMO surfaces delocalize similarly in both dyes, the HOMO surfaces extend over the whole BDT₁ moiety in **CR29** and to a noticeable lesser extent over BDT in **CR52**. Therefore, the larger overlap between the two frontier orbitals in **CR29** translates into the higher transition probability. Overall, **CR29** displays a better overlap with the visible spectrum, showing, at the same time, higher molar absorptivities.

Both **CR29** and **CR52** are highly luminescent only in toluene solution (Figure 5). The broad featureless emission profiles, which mirror the lowest energy absorption bands,



Figure 5. Normalized absorption (solid lines) and emission (dashed lines) spectra of dyes **CR29** (top) and **CR52** (bottom) in toluene solution recorded in the presence of TFA (black lines) and Et_3N (grey lines).

and the large Stokes shift (ca. 130–140 nm) are indicative signatures of the CT nature of the emissive state.

The excitation spectra match, in shape and intensity, the absorption spectra, hence the luminescence stems from radiative emission of the molecular species. In all other solvents the emission is completely quenched, possibly suggesting a strong interaction with the solvents that triggers nonradiative relaxation pathways.^[14]

The optical properties of **CR29** and **CR52** were also investigated upon addition of Et_3N to the solutions (Figure 5). A blueshift in absorption maximum was observed in this case when compared to the absorption spectra in the presence of TFA. This could be related to the deprotonation/protonation equilibrium of the carboxylic acid group. In fact, the addition of base shifts the dye from its free carboxylic acid form (COOH) to the carboxylate form (COO⁻), drastically reducing the strength of the acceptor moiety and, at the same time, the donor-acceptor interaction within the dye.^[14] The protonation of the amine unit by the TFA can be excluded on the basis of the pK_a value

of the conjugate acid of the triarylamine group, which is -5, whereas that of TFA is 0.5.

In all of the solvents (see Figure S5 and S6 in the Supporting Information), we found that the CT absorption band in the carboxylate form blue shifts, on average, 35–50 nm compared to the protonated form (see Figure 5 for toluene solution). This destabilization of the CT character is also evident in the emission spectra; in fact, **CR29** emits at 624 nm in the protonated form and at 577 nm in the deprotonated form; **CR52** emits respectively at 620 and 580 nm.

The electron transfer properties of chromophores **CR29** and **CR52** have been studied by cyclic voltammetry together with those of the corresponding parent molecules **BDT**₁ and **BDT**. Selected results are reported in Table 4, see also Figures 6 and 7.

The angular **BDT** and the linear BDT_1 fragments feature similar CV patterns, with chemically irreversible first oxidation and first reduction peaks (Figure 6), indicating that the corresponding radical cation and radical anion undergo

Table 4. Selected CV features for chromophores CR52 and CR29 and parent molecules BDT and BDT₁, together with linear α, α -bithiophene (T₂) as a benchmark, and corresponding HOMO and LUMO energy levels and gaps.

	$E_{\rm Ic,onset}$ V(Fc ⁺ Fc)	$E_{\rm Ic,p}$ V(Fc ⁺ Fc)	$E_{\text{Ia,onset}}$ V(Fc ⁺ Fc)	$E_{\text{Ia,p}}$ V(Fc ⁺ Fc)	$E_{\mathrm{IIa,p}}$ V(Fc ⁺ Fc)	E _{LUMO} (onset) [eV]	E _{HOMO} (onset) [eV]	E _g (onset) [eV]	E _{LUMO} (max) [eV]	E _{HOMO} (max) [eV]	$E_{\rm g}$ (max) [eV]
T ₂ ^[a] BDT ^[b]	-2.82	-2.84 -3.00	0.97	0.88 1.10		-1.98	-5.77	≈3.6 3.79	-1.96 -1.80	-5.68 -5.90	3.72 4.10
BDT ₁ ^[b] CR52 ^[c] CR29 ^[c]	-2.75 -2.04 -1.86	-2.93 -2.13 -1.96	0.87 0.15 0.14	1.01 0.28 0.26	0.84 0.85	-2.05 -2.76 -2.94	-5.67 -4.95 -4.94	3.62 2.19 2.00	-1.87 -2.67 -2.84	-5.81 -5.08 -5.06	3.94 2.41 2.22

[a] From Refs.^[15a] (anodic peak, in $CH_2Cl_2 + 0.1 \text{ M TBAPF}_6$) and Refs.^[20] (cathodic peak, in dimethylacetamide + 0.1 M TBABr), here both referred to Fc⁺|Fc. [b] In $CH_3CN + 0.1 \text{ M TBAP}$, at 0.2 V s⁻¹, referred to Fc⁺|Fc (this work). [c] In $CH_2Cl_2 0.1 \text{ M TBAP}$, at 0.2 V s⁻¹, referred to Fc⁺|Fc (this work).



Figure 6. CV features for BDT and BDT₁ in CH₃CN + 0.1 M TBAP, at 0.2 V s⁻¹ scan rate, with ohmic drop compensation.



Figure 7. CV features for chromophores CR52 and CR29 in CH₂Cl₂ + 0.1 M TBAP, on GC, at 0.2 Vs⁻¹ scan rate, with ohmic drop compensation.

chemical reactions. BDT_1 has its first oxidation peak at 1.01 V and first reduction at -2.93 V. In contrast, angular BDT oxidizes at 1.10 V and reduces at -3.00 V. In this respect the π conjugation is more effective in the linear isomer than in the angular isomer. The conjugation efficiency of **BDT₁** appears comparable to, or slightly lower than, the linear 2,2'-bithiophene (Table 4).^[15]

From the onset and peak potentials for the first reduction and first oxidation, LUMO and HOMO energies can be estimated from the equations reported in the Supporting Information (Equations S1a, S1b, S2a, S2b),^[16,17] and are ultimately based on the absolute value for the normal hydrogen electrode (NHE), which was critically assessed in a fundamental review paper.^[18] The resulting values, together with the corresponding energy gaps $E_{\rm g}$, are reported in Table 4 together with their counterparts obtained by absorption spectroscopy.

The electrochemical E_{g} values show good consistency with the spectroscopic data, adopting the onset criterion. It is worth noting that, although the electrochemical and spectroscopic $E_{\rm g}$ values are often correlated, they refer to different processes (respectively electron transfer from/to the molecule vs. electron promotion between different states), which can be affected to different extents by solvent interactions and other parameters.

Chromophores CR29 and CR52, which only differ in having an angular or a linear BDT linker, have similar CV patterns. In particular, as shown in Figure 7, two nearly merging two-peak systems, partially chemically reversible, can be observed for oxidations, followed by a complex multielectron irreversible shoulder on the background. First oxidations (0.26 V for CR29 and 0.28 V for CR52) must be localized on the electron-rich triarylamino site, as evidenced by DFT calculations, and are consistent with literature data.^[19] The localized nature of the electron transfer, together with the distance from the BDT₁ or BDT building block explains the nearly equal oxidation potential in the two chromophores.

The first reduction accounts for a monoelectronic, electrochemically reversible peak at -1.96 V for CR29 and -2.13 V for CR52, which are considerably less negative potentials than in the parent BDT molecules. The observed reductions correspond to localized processes involving the electron-poor terminal double bond carrying a cyanoacrylic group. The immediately adjacent **BDT₁/BDT** moiety affects these processes such that the reduction peak of CR29 is significantly less negative than that of CR52. Moreover, the reduction peak appears to be electrochemically reversible (i.e., accounting for a fast electron transfer) in both cases, but is chemically reversible only in the linear form.

Remarkably, the lower E_g value of **BDT₁** with respect to that of BDT is reflected in the corresponding dyes, such that **CR29** has a smaller E_g value than **CR52**. The 0.19 eV difference between the two dyes mostly arise from the difference in the reduction peak potentials (i.e., in LUMO energy). This feature is in perfect agreement with the trend (not the absolute values) of the theoretical computations. This is less evident in the spectroscopic approach, possibly as a consequence of the width and complexity of the first absorption band.

It is worth noting that the calculated HOMO-LUMO energies (Table 1) and trends are fully consistent with electrochemical measurements (Table 4), showing a HOMO (LUMO) onset at -4.94/-4.95 (-2.94/-2.76) eV (Table 4) for

With these photovoltaic parameters, efficiencies of 5.14

and 3.63% are calculated for the **CR29** and **CR52** dyes. In both cases, these results were obtained by using chenod-

CR29 and **CR52**, respectively, which are comparable to the calculated values at -4.73/-4.70 (-2.83/-2.74) eV.

1.4. Solar Cell Performance and Charge Generation Processes

Liquid electrolyte based DSSC were fabricated and tested under AM 1.5 conditions (Figure 8a). **CR29** gave the best results in terms of photocurrent (10.65 mA/cm²) and open-circuit voltage (0.71 V) with respect to **CR52** (7.97 mA/cm² and 0.67 V), whereas the same FF values are found (0.68, see Table 5).



Figure 8. Current density vs. voltage under AM1.5 simulated sunlight (100 mW/cm²) illumination for: (a) **CR29** (black line) and **CR52** (dashed line) in liquid DSSC. A commercial electrolyte containing 1-butyl-3-methylimidazolium iodide, iodine, guanidinium thiocyanate, and *tert*-butylpyridine in a mixture of valeronitrile and acetonitrile, with 0.06 M LiI added, was used. (b) **CR29** (black line) and **N719** (dashed line) in solid state DSSC.

Table 5. Photovoltaic	performance	of CR2	29 and	CR52
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Dye	$J_{\rm sc} [{\rm mA/cm^2}]$	$V_{\rm oc}$ [V]	FF	η [%]
CR29 ^[a]	10.65	0.71	0.68	5.14
CR29 ^[b]	5.65	0.78	0.54	2.47
CR52 ^[a]	7.97	0.67	0.68	3.63
N719 ^[b]	2.10	0.77	0.56	0.95

[a] Liquid electrolyte DSSCs. [b] Solid State DSSCs.

eoxycholic acid (CDCA) in the dye solutions as an antiaggregant agent.^[21] Indeed, it has been reported that organic dyes often suffer from aggregation issues, leading to poor charge injection and consequent reduction in the efficiency of the device.^[22] We also observed these problems with the CR29 dye. In fact, without using CDCA, a maximum of 1.1% efficiency was obtained, with poor J_{sc} and $V_{\rm oc}$ values of respectively 3.5 mA/cm² and 0.56 V. Another important additive that can be used to optimize cell performance is the LiI in the electrolyte solutions. It has been noted that Li ions are able to downshift the TiO₂ conduction band, facilitating the charge injection process and then improving the generated photocurrent.^[23] For the CR29 dye, without using LiI in the electrolyte solution, we obtained an efficiency of 3.35%, which is considerably lower with respect to the optimized cell (see the Supporting Information). We measured a J_{sc} value of 7.04 mA, leading to a decrease in the efficiency, whereas the $V_{\rm oc}$ (0.71 V) and FF (0.67) values were not influenced by the additive. The cell experimental results are encouraging when compared to solar cells made with the prototype N719 ruthenium dye under similar conditions (i.e., employing the sensitization procedure optimized for N719), the output efficiency yield of which was 6.36% (see the Supporting Information). It is also worth noting here the importance of careful selection of the spacer unit in a donor-acceptor dye architecture. In fact, as already anticipated by the theoretical and spectroscopic analysis of the chromophore, the use of the BDT_1 conjugated spacer allows stabilization of the CT transition together with an improvement of its absorption cross-section, which is translated, in terms of device performance, in an improvement of thee solar cell photocurrent.

The most efficient molecule, CR29, has also been tested in a solid state device in which a molecular hole transporter, 2,20,7,70-tetrakis(bis-p-methoxyphenylamino)-9,90-spirobifluorene (spiro-OMe TAD) was used instead of the liquid electrolyte. The solar cell, although not fully optimized in terms of device architecture (i.e., lithium salts and tert-butylpyridine concentration, device thickness), clearly shows the full potential of this metal-free dye. Figure 8b shows the device characteristic compared to the output of a device that uses the conventional N719 ruthenium dye, and in Table 5 the figures of merit of the solar cells are reported. Furthermore, in this case, it is clear that the strong enhancement in photocurrent drives the improvement in the devices performances, which is a result of an enhanced ability of the fully organic dye to harvest sunlight, together with good charge generation processes.

Some preliminary studies have been carried out by using time-resolved photoluminescence spectroscopy to investigate the charge generation processes (i.e., electron transfer from the dye to the TiO_2 and hole transfer to the spiro OMeTAD).^[24] All samples present the same additives used in the actual device (CDCA, Li-TFSI and 4-*tert*-butylpyridine) because it is known that they can strongly influence

the metal oxide and dye energetics and the kinetics of the main device working mechanisms.^[25] In Figure 9a the photoluminescence (PL) emission from the dye chemisorbed on a TiO₂ and ZrO₂ mesoporous substrates is reported. The latter is a high band gap oxide that does not allow for electron transfer from the dye to the metal oxide. The decays have been fitted by a stretched exponential function to extract the average electron injection lifetime on the TiO₂ ($\tau_{inj} \approx 15 \text{ ps}$) and the average exciton lifetime on the ZrO₂ ($\tau_{obs} \approx 71 \text{ ps}$) and finally estimate the electron injection efficiency (η_{inj}) according to the following expression.^[24]

$$\eta_{\rm inj} = \frac{1/\tau_{\rm inj}}{1/\tau_{\rm inj} + 1/\tau_{\rm obs}}$$



Figure 9. Time-resolved photoluminescence (PL) spectra from (a) **CR29** dye adsorbed on mesoporous films of ZrO_2 and TiO_2 ; (b) **CR29** adsorbed on mesoporous films of ZrO_2 with and without spiro-oMeTAD infiltrated. All samples present the same additives used in the fabrication of the solid state DSSC. Decays are taken at 700 nm, the peak of the PL spectra. Excitation at 450 nm.

We calculate an electron injection efficiency of 76%. In Figure 9b the PL emission from the dye chemisorbed on a ZrO_2 substrate is shown with and without spiro OMeTAD to estimate the hole transfer efficiency as described above. The noninjecting substrate is used to disentangle the hole-transfer and electron-transfer mechanisms in the PL quenching experiment. A hole-transfer efficiency of the order of 53% has been found. The hole-transfer yield is likely underestimated because measurements were per-



formed with the dye in contact with a high band gap metal oxide, therefore, the charge-transfer process starts from a bound singlet exciton photogenerated on the dye, whereas, in a working device, the dye can be already oxidized thanks to efficient electron injection to the TiO_2 layer.

Conclusions

We have reported on the design and synthesis of two novel dyes, CR29 and CR52, as photosensitizers for DSSCs. The dyes are endowed with two isomeric benzodithiophene units (**BDT**₁ and **BDT**) as π -spacers. Their synthesis has been achieved in good yields by using standard synthetic procedures and the dyes have been analytically characterized. On the basis of DFT calculations, UV/Vis absorption and emission studies, and cyclovoltammetric characterization, it has been possible to show that the **BDT**₁ π bridge appears to be more suitable than BDT in donoracceptor molecules on the basis of its better conjugation, to effectively couple the triarylamine donor unit and the cyanoacetic acceptor moiety. DSSC fabricated from the BDT₁-containing chromophore (CR29) exhibits promising performances, especially in the solid state device in which the use of a high extinction coefficient dye is a demanding requirement. SS-DSSCs fabricated and sensitized with CR29 exceed the performance of a solar cell using a standard ruthenium complex N719.

Further developments and exploitation of this work will consider the use of less conventional donor and acceptor groups, to establish, in a homogeneous series of organic dyes based on BDT_1 , the structure–performance relationships.

Experimental Section

Reagents and Methods: All reagents and solvents were obtained from highest grade commercial sources and used without further purification unless otherwise stated. Column chromatography was carried out using silica gel 60 (70-230 mesh, Merck). ¹H NMR spectra were acquired with a Bruker AVANCE DRX-400, a Bruker AC300, or an AMX 300 MHz spectrometer; chemical shifts (δ) are reported in parts per million relative to the solvent residual peak ([D₆]acetone, [D₆]DMSO, CDCl₃). IR spectra were recorded with a Fourier Bruker Vector 22 FT; UV spectra were recorded with a Jasco V-520 or Agilent 8453 UV/Vis spectrophotometer in a range of λ from 190 to 800 nm at room temperature. Steady-state emission and excitation spectra were measured using a Horiba scientific FluoroLog 3. HRMS spectra were recorded with a Bruker Daltonics ICR-FTMS APEX II. Melting points were obtained with a Büchi B-540 melting point apparatus and are uncorrected. HPLC analyses were performed with an Agilent 1100 series equipped with a PDA detector and a reverse-phase ZORBAX Eclipse XBD-C18 column (4.6×150 mm, 5 µm particle size); samples were analyzed with 1 mL/min acetonitrile/water (80:20) with 0.1% TFA. CR29 and CR52 samples for cell fabrication were assessed by HPLC analysis and the purity was estimated to be over 98%.

({4-[Bis(4-methoxyphenyl)amino]phenyl}methyl)triphenylphosphonium Bromide (1): Obtained with a slightly modified literature procedure.^[26] A solution of 4-[bis(4-methoxyphenyl)amino]benzyl alcohol (374.5 mg, 1.12 mmol) and PPh₃·HBr^[27] (421.5 mg, 1.23 mmol) in CHCl₃ (6 mL) was heated to reflux whilst stirring for 4 h. The solvent was then evaporated and the residue was treated with Et₂O (10 mL). The phosphonium salt, precipitated from the solution as a white solid, was filtered to give 1 (700 mg, 95%). ¹H NMR (300 MHz, [D₆]acetone): δ = 3.76 (s, 6 H), 5.30 (d, *J* = 14.2 Hz, 2 H), 6.52 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.9 Hz, 4 H), 6.88–6.95 (m, 2 H), 6.99 (d, *J* = 8.9 Hz, 4 H), 7.70–7.76 (m, 6 H), 7.81–7.91 (m, 9 H) ppm. ³¹P NMR (121 MHz, CDCl₃): δ = 23.09 ppm.

6-(2-{4-[Bis(4-methoxyphenyl)amino]phenyl}ethenyl)benzo[1,2-b:4,5b' dithiophen-2-carbaldehyde (4): A solution of 1 (100 mg, 0.15 mmol) in DMF (4 mL) was slowly added, whilst stirring at room temperature, to a slurry of 2,6-benzo[1,2-b:4,5-b']dithiophenedicarbaldehyde (2;^[28] 50 mg, 0.20 mmol), 18-crown-6 ether (3 mg), and anhydrous K₂CO₃ (32 mg, 0.30 mmol) in DMF (4 mL). The resulting orange solution was stirred overnight at room temperature. The solution was then poured into water (10 mL) and extracted with dichloromethane $(4 \times 10 \text{ mL})$. The organic phase was washed with water (20 mL), dried with Na₂SO₄, and filtered. After evaporation of the solvent, the crude dark-orange product was purified by silica gel column chromatography (CH₂Cl₂/hexane, 9:1) to afford 4 (51 mg, 63%) as a red solid; m.p. 212–214 °C (dec). ¹H NMR (300 MHz, [D₆]DMSO): δ = 3.73 (s, 6 H), 6.72 (d, J = 8.6 Hz, 2 H), 6.92 (d, J = 8.9 Hz, 4 H), 6.97 (d, J = 16.4 Hz, 1 H), 7.05 (d, J = 8.9 Hz, 4 H), 7.39 (d, J = 16.4 Hz, 1 H), 7.44 (d, J =8.6 Hz, 2 H), 7.45 (s, 1 H), 8.41 (s, 2 H), 8.6 (s, 1 H), 10.11 (s, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 55.18, 114.96, 117.15, 118.16, 118.38, 119.06, 119.99, 121.68, 124.35, 126.95, 127.37, 127.58, 127.73, 127.86, 129.71, 132.53, 135.53, 139.60, 143.12, 148.35, 155.97, 185.95 ppm. IR (nujol): $\tilde{v} = 1670 (v_{CO}) \text{ cm}^{-1}$. HRMS (EI): calcd. for C₃₃H₂₅NO₃S₂ 547.127588; found 547.126650. UV/Vis (CH₃CN): λ_{max} (ϵ , M^{-1} cm⁻¹) = 298 (1.8 × 10⁴), 344 (2.1×10^4) , 451 (3.6×10^4) nm.

2-Cyano-3-[6-(2-{4-{bis(4-methoxyphenyl)amino}phenyl}ethenyl)benzo[1,2-b:4,5-b']dithiophen-2-yl]propenoic Acid (CR29): Cyanoacetic acid (20.0 mg, 0.24 mmol) and piperidine (5 mg, 0.05 mmol) were added to a suspension of 4 (70 mg, 0.13 mmol) in CH₃CN (10 mL). The reaction mixture was stirred for 4 h at 80 °C. The solvent was then evaporated and the residue was taken up with a mixture HCl 0.1M (6 mL) and hexane (4 mL) and filtered to afford CR29 (70 mg, 95%) as a red solid; m.p. 258-260 °C (dec). ¹H NMR (300 MHz, [D₆]DMSO): $\delta = 3.76$ (s, 6 H), 6.74 (d, J =8.5 Hz, 2 H), 6.90–6.96 (m, 5 H), 7.05 (d, J = 9 Hz, 4 H), 7.36– 7.46 (m, 3 H), 7.96 (s, 1 H), 8.23 (s, 2 H), 8.37 (s, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 55.13, 101.17, 114.88, 115.84, 116.44, 118.26, 118.50, 119.02, 119.08, 121.51, 126.83, 126.95, 127.27, 127.55, 127.68, 127.81, 132.05, 135.06, 135.28, 135.35, 136.97, 139.06, 139.33, 140.89, 146.50, 147.12, 148.63, 155.98, 163.09 ppm. IR (nujol): $\tilde{v} = 3402 (v_{OH}), 2360 (v_{CN}), 1569 (v_{CO}) \text{ cm}^{-1}$. HRMS (ESI): calcd. for $C_{36}H_{25}N_2O_4S_2 [M - H]^- 613.12557$; found 613.12579. UV/Vis (CH₂Cl₂, 6×10^{-5} M): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 370 (2.2×10^4) , 460 (2.1×10^4) nm; EtOH $(5 \times 10^{-5} \text{ M})$: λ_{max} (ε , $M^{-1}cm^{-1}$ = 368 (7.2×10³), 443 (1.2×10⁴) nm; THF (5×10⁻⁵ M): $\lambda_{\text{max}} (\varepsilon, \text{ m}^{-1} \text{ cm}^{-1}) = 375 (2.9 \times 10^4), 478 (3.7 \times 10^4) \text{ nm}; \text{ toluene}$ $(5.9 \times 10^{-5} \text{ M}): \lambda_{\text{max}} (\varepsilon, \text{ M}^{-1} \text{ cm}^{-1}) = 371 (1.5 \times 10^{4}), 440 (1.3 \times 10^{4})$ nm; CH₃CN (5.7×10⁻⁵ м): λ_{max} (ϵ , M^{-1} cm⁻¹) = 371 (3.6×10⁴), 469 (3.9×10^4) nm.

7-(2-{4-[Bis(4-methoxyphenyl)amino]phenyl}ethenyl)benzo[1,2-b:4,3*b'*]**dithiophen-2-carboxy aldehyde (5):** Following the same procedure used for the synthesis of **4**, phosphonium salt **1** (0.30 mmol) was treated with benzo[1,2-b:4,3-b']-2,7-dithiophenedicarbaldehyde (3;^[29] 0.36 mmol) in DMF (6 mL). A crude dark-orange product was obtained that was purified by silica gel column chromatography (CH₂Cl₂/hexane, 9:1) to afford **5** (76 mg, 46%) as a red solid; m.p. 160–162 °C. ¹H NMR (300 MHz,CDCl₃): δ = 3.81 (s, 6 H), 6.83–6.91 (m, 6 H), 7.01 (d, *J* = 15.9 Hz, 1 H), 7.03–7.09 (m, 4 H), 7.13 (d, *J* = 15.9 Hz, 1 H), 7.32 (d, *J* = 8.7 Hz, 2 H), 7.5 (s, 1 H), 7.70 (d, *J* = 8.7 Hz, 1 H), 7.80 (d, *J* = 8.7 Hz, 2 H), 7.5 (s, 1 H), 10.12 (s, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 55.51, 114.83, 117.15, 118.81, 119.40, 119.9, 122.54, 126.97, 127.37, 127.52, 128.17, 131.64, 133.28, 135.74, 136.97, 140.57, 143.03, 146.10, 148.95, 156.34, 184.09 ppm. IR (nujol): \tilde{v} = 1646 (vCO) cm⁻¹. HRMS (EI): calcd. for C₃₃H₂₅NO₃S₂ 547.12758; found 547.127588. UV/Vis (CH₃CN, 6.3 × 10⁻⁵ M): λ_{max} (ε, m⁻¹ cm⁻¹) = 299 (1.84 × 10⁴), 354 (2.72 × 10⁴), 439 (3.42 × 10⁴) nm.

2-Cyano-3-[7-(2-{4-[bis(4-methoxyphenyl)amino]phenyl}ethenyl)benzo[1,2-b:4,3-b']dithiophen-2-yl]acrylic Acid (CR52): Synthesized following the same procedure used for CR29, starting from 5 (70 mg, 0.13 mmol) to afford CR52 (46 mg, 55%) as a red solid; m.p. 198–200 °C. ¹H NMR (300 MHz, $[D_7]DMF$): $\delta = 3.80$ (s, 6 H), 6.74 (d, J = 8.5 Hz, 2 H), 6.95 (d, J = 9 Hz, 4 H), 6.97 (d, J = 16.4 Hz, 1 H), 7.08 (d, J = 9 Hz, 4 H), 7.42 (d, J = 16.4 Hz, 1 H), 7.47 (d, J = 8.5 Hz, 2 H), 7.45 (s, 1 H), 8.35 (s, 2 H), 8.47 (s, 1 H), 8.58 (s, 1 H), 8.64 (s,1 H) ppm. $^{13}\mathrm{C}$ NMR (75 MHz, [D₇]DMF): δ = 55.78, 115.67, 116.84, 119.57, 119.73, 121.23, 123.60, 127.97, 128.56, 128.76, 132.17, 133.59, 135.92, 136.50, 140.76, 146.84, 147.93, 149.85, 157.32, 164.13 ppm. IR (nujol): $\tilde{v} = 3393$ (v_{OH}), 2342 (v_{CN}) , 1560 (v_{CO}) cm⁻¹. HRMS (ESI): calcd. for $C_{36}H_{25}N_2O_4S_2$ [M – H]⁻ 613.12612; found 613.12504. MS (ESI): $m/z = 614.3 \text{ [M]}^{-}$, 570.4 (M - CO₂), 555.4 [M - CH₃]. UV/Vis (EtOH, 3.18×10^{-5} M): λ_{max} (ϵ , M^{-1} cm⁻¹) = 391 (3.8×10^{4}), 441 (2.7×10⁴) nm; THF (3.21×10⁻⁵ M): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 394 (4.2 × 10⁴), 460 (2.6 × 10⁴) nm; toluene (3.03 × 10⁻⁵ M): λ_{max} (ε , $M^{-1} cm^{-1}$) = 399 (3.8 × 10⁴), 478 (2.1 × 10⁴) nm; CH₃CN $(2.97 \times 10^{-5} \text{ M})$: $\lambda_{\text{max}} (\varepsilon, \text{ M}^{-1} \text{ cm}^{-1}) = 393 (4.2 \times 10^4), 451 (2.6 \times 10^4)$ nm; CH₂Cl₂ (3.21×10⁻⁵ M): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 399 (5.6×10⁴); 486 (2.74×10^4) nm.

Electrochemistry: Chromophores **CR29** and **CR52**, and the corresponding parent molecules BDT_1 and BDT were characterized by cyclic voltammetry at potential scan rates typically ranging from 0.05 to 2 V s^{-1} , in a 4 cm³ minicell with 0.5–0.75 mM solutions in CH₂Cl₂ (chromophores) and CH₃CN (parent molecules) with 0.1 M TBAP as the supporting electrolyte, deaerated by N₂ purging. In particular, parent molecules required solvent CH₃CN to allow observation of the first reduction peaks, located at very negative potentials. On the other hand, the chromophores were hardly soluble in CH₃CN; however, in this case, the cathodic potential window of CH₂Cl₂, granting good solubility, was sufficient, albeit narrower than in CH₃CN, on account of the much more positive reduction peak potentials.

The experiments were carried out with an AUTOLAB PGSTAT 12(8) potentiostat of EcoChemie (Utrecht, The Netherlands) run by a PC with the GPES 4.9 software of the same manufacturer.

The working electrode was a glassy carbon GC disk embedded in Teflon (Amel, 0.071 cm^2). The optimized polishing procedure involved surface treatment with a synthetic diamond powder of 1 mm diameter (Aldrich) on a DP-Nap wet cloth (Struers).

The operating reference electrode was aqueous saturated calomel (SCE), but the experimental peak potentials have been normalized vs. the Fc⁺|Fc redox couple (the intersolvental redox potential reference currently recommended by IUPAC),^[16,17] having a redox potential of 0.39 V (in CH₃CN) or of 0.495 V (in CH₂Cl₂) vs. the operating SCE reference electrode. The counter electrode was a

platinum disk embedded in glass. The ohmic potential drop was compensated for by the positive feedback technique.^[18]

Computational Methods: Calculations on the structure and simulated UV/Vis absorption spectra were performed using density functional theory (DFT), and its time-dependent formulation (TDDFT), as implemented in Gaussian program suite.^[30] The ground-state geometry for the protonated dyes were optimized in gas-phase, within the B3LYP functional^[31] using a 6-31G* basis set.^[12] At the optimized ground-state geometries TDDFT (B3LYP and MPW1K/6-31G*)^[13] excited state calculations were performed in the gas phase as well as in acetonitrile, adopting the nonequilibrium conductor-like polarizable continuum model (CPCM).^[32] This computational setup has previously been shown to adequately describe the electronic and optical properties of similar push-pull dyes.^[33,34]

Liquid Electrolyte Solar Cell Assembly: Fluorine-doped tin oxide (FTO) glass (TEC-15/2.2 mm thickness, Solaronix) was used for transparent conducting electrodes. The substrate was first cleaned in a ultrasonic bath using a detergent solution, acetone, and ethanol (each step 15 min long). The FTO glass plates were immersed into a 40mm aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. The Dyesol 18NR-AO TiO₂ paste was spread on the FTO glass plates by using the doctor blade technique. The TiO₂ coated electrodes (active area 0.2 cm²) were gradually heated under air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and 500 °C for 15 min. After the sintering process, the TiO₂ film was treated with 40mM TiCl₄ solution, rinsed with water and ethanol. The electrodes were heated at 500 °C for 30 min and after cooling (80 °C) were immersed for six hours in sensitizing baths [CH₃CN solutions of the CR29/52 dyes in 0.2 mM concentration, containing 3 mM 3a,7a-dihydroxy-5b-cholic acid (CDCA)].

Counter electrodes were prepared by coating with a drop of $[H_2PtCl_6]$ solution (2 mg of Pt in 1 mL of ethanol) a FTO plate (TEC 15/2.2 mm thickness, Solaronix) and heating at 400 °C for 15 min. The TiO₂ sensitized photoanode and Pt counter electrode were assembled into a sealed sandwich-type cell by a hot-melt ionomer film (Surlyn, 25 µm thickness, Dyesol).

An Iolitech ES-0004 HP electrolyte was used, containing 1-butyl-3-methylimidiazolium iodide, iodine, guanidinium thiocyanate, and *tert*-butylpyridine in a mixture of valeronitrile and acetonitrile, with 0.06M LiI added. The hole was then sealed by applying a Surlyn patch and a cover glass and finally a conductive Ag-based paint was deposed at the electrical contacts.

Solid-State Solar Cell Assembly: FTO-coated glass sheets (15 Ω /sq Pilkington) were etched with zinc powder and HCl (2 M) to obtain the required electrode pattern. The sheets were then washed with soap (Hellmanex at 2% in water), deionized water, acetone, methanol, and finally treated under an oxygen plasma for 10 min to remove the last traces of organic residues. The FTO sheets were subsequently coated with a compact layer of TiO₂ (100 nm) by aerosol spray pyrolysis deposition at 450 °C, using oxygen as the carrier gas.

Standard Dyesol TiO₂ paste was previously diluted 1:3.5 in ethanol and ultrasonicated until complete mixing. The paste was then applied by means of the doctor blade technique using scotch tape and a pipette on the TiO₂ compact layer coated FTO sheets to get a TiO₂ average thickness of 1.8 μ m.

The sheets were then slowly heated to 550 °C (ramped over 1.5 hours) and baked at this temperature for 30 min in air. After cooling, the slides were cut to size and soaked in 15 mM TiCl₄ in a



water bath and oven-baked for 1 h at 70 °C. After rinsing with water, ethanol, and drying in air, they were subsequently baked at 550 °C for 45 min in air, then cooled to 70 °C and finally introduced into a dye solution [0.3 mM in CH₃CN/THF (10:1) containing 3 mM 3a,7a-dihydroxy-5b-cholic acid (CDCA)] for 16 h. The Spiro-OMeTAD was dissolved in chlorobenzene at a concentration of 90 mg/mL; a solution of lithium bis(trifluoromethylsulfonyl)imide salt (Li-TFSI) (0.04M in CH₃CN) and 4-tert-butylpyridine was added to the Spiro-OMeTAD solution and spin-coated at 700 rpm for 60 s. Spin coater rotation was activated 45 seconds after dispensing the solution onto the substrate to promote effective infiltration of Spiro-OMeTAD inside the mesoporous TiO₂ layer. The films were then placed in a thermal evaporator where 80 nm thick silver electrodes were deposited through a shadow mask under high vacuum (10⁻⁶ mbar), to obtain pixels of an active area of ca. 0.08 cm².

Photovoltaic Measurements: Photovoltaic measurements were recorded under an AM 1.5 solar simulator equipped with a Xenon lamp (LOT-ORIEL LS 0106). The power of incoming radiation, set at 100 mW/cm², was checked by a piranometer. J–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital sourcemeter, under the control of dedicated LabTracer 2.0 software. A black shading mask was employed to avoid overestimation of the measured parameters.^[35]

Time-Resolved Photoluminescence: Time-resolved photoluminescence spectra were recorded with a Hamamatsu Picosecond Fluorescence Lifetime system based on a Strek camera with 2 ps time response. Excitation (450 nm) was provided by a 150 fs ultrafast laser oscillator (Chamaleon, Coherent Inc.); emisson signals were detected at 700 nm. All samples were measured at room temperature in a vacuum chamber (10^{-4} mbar).

Supporting Information (see footnote on the first page of this article): Extended calculations, simulated absorption spectra, additional solar cell parameters, UV absorption of BDT and BDT₁, optical absorptions upon acid and base treatment of CR29 and CR52. UV absorption of CR29 on TiO₂.

Acknowledgments

V. R. thanks Marcelo Alcocer and Ajay Ram Srimath Kandada for support in the transient optical spectroscopy experiments. P. S. and F. D. A. thank MIUR-PRIN 2008 and CNR-EFOR for financial support. E. L. and S. M. thank the Fondazione Cariplo (grant number 2008-2205) and the University of Milan for a Ph.D. fellowship (E. L.). C. B. thanks CNR-PM.P04.012 for financial support. The authors thank Rossana Colombo for some experimental work.

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Received: July 18, 2012 Published Online: November 22, 2012