

Photoinduced electron transfer in a fullerene–oligophenylenevinylene dyad

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A dialkylamino-substituted oligophenylenevinylene (OPV) derivative bearing a fullerene subunit (F–D) has been prepared. The electrochemical properties of F–D have been investigated by cyclic voltammetry. Whereas the first reduction is centered on the C₆₀ unit, the oxidation is centered on the dialkylamino subunit of the OPV rod. In F–D, both the OPV and the fullerene-centered fluorescence bands are quenched and this suggests the presence of photoinduced electron transfer from the amino-substituted OPV to the carbon sphere. By means of bimolecular quenching experiments, transient absorption spectral fingerprints of the radical cationic species have been detected in the VIS (670 nm) and NIR (1300–1500 nm) regions, along with the much weaker fullerene anion band at $\lambda_{\text{max}} = 1030$ nm. Intramolecular photoinduced electron transfer occurs in the investigated dyad and a relatively long-lived charge-separated state has been detected, with a lifetime of 135 and 85 ns in toluene and benzonitrile, respectively. The longer lifetime in the less polar solvent suggests a Marcus inverted region behavior for the charge recombination process.

Introduction

Owing to their low reduction potentials and low reorganization energy in electron-transfer reactions, fullerene derivatives are outstanding electron acceptors in photoactive molecular devices.¹ Actually, an impressive amount of work has been devoted to the development of molecular systems in which C₆₀ is covalently linked to electron donors.¹ As part of this research, hybrid compounds combining the carbon sphere with π -conjugated oligomers are of particular interest.² Effectively, their peculiar electronic properties led to the development of promising molecular materials for photovoltaic applications.³ In this particular case, the occurrence of photoinduced electron transfer is of fundamental importance as charges have to be produced upon light absorption to generate the photocurrent. However, for C₆₀–(π -conjugated oligomer) hybrid systems, the anticipated electron transfer process is in competition with an ultrafast energy transfer.⁴ Hence, fullerene derivatives are also excellent energy acceptors and the low-lying fullerene singlet and triplet excited states are quite often the final products of the photoinduced processes.⁴ Sometimes, however, the initial energy transfer event can be followed by an electron transfer when the energy level of the

charge-separated state is lower than that of the fullerene singlet. Indeed, such a favorable thermodynamic driving force is mainly dependent on the donating ability of the conjugated oligomer associated to the fullerene acceptor. For moderate donors, the charge-separation process shows a strong solvent polarity dependence. For example, Hummelen, Janssen and co-workers have reported the photophysical properties of an oligophenylenevinylene (OPV)–C₆₀ conjugate in solvents of different polarity.⁵ In apolar solvents such as toluene, the charge-separated state is higher in energy than the first fullerene singlet and triplet excited states. Therefore, the light energy absorbed by the OPV fragment, promptly conveyed to the fullerene lowest singlet excited state *via* energy transfer, cannot yield charge separation anymore. In contrast, the energy of the charge-separated state drops below that of the first fullerene singlet excited state in more polar solvents allowing occurrence of electron transfer after the initial energy transfer event. Similar findings have been reported by Martin, Guldi and co-workers⁶ for a series of oligonaphthylenevinylene–fullerene dyads and by us for fullerene derivatives covalently linked to OPV fragments⁷ or dendritic wedges.⁸ In this paper, we now report a new C₆₀–oligophenylenevinylene (OPV) derivative in which the OPV unit has been functionalized with a dialkylamine group to improve its donating ability.⁹ As a result, photoinduced electron transfer is observed upon the initial energy transfer whatever the solvent.

Results and discussion

Synthesis

In the design of the C₆₀–OPV conjugate, we have decided to introduce a spacer unit between the two photoactive moieties

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in order to prevent fast charge recombination upon electron transfer and thus to facilitate the observation of the charge-separated state. The synthesis is based on the esterification reaction of a fullerene carboxylic acid building block with an OPV derivative bearing one hydroxy group. In the first synthetic approach, we have prepared OPV oligomer **D** bearing a terminal bromobenzene subunit (Scheme 1). The latter should give us access to the targeted OPV building block with an alcohol group by lithiation followed by quenching with formaldehyde.

Reaction of 4-bromophenol (**1**) with 2-bromoethanol under Williamson conditions (K_2CO_3 , DMF) gave alcohol **2** in 83% yield. Subsequent treatment with CBR_4 - PPh_3 in THF afforded bromide **3** in 70% yield. Alkylation of 4-hydroxybenzaldehyde with **3** gave aldehyde **4** in 88% yield. Reaction of **4** with phosphonate **5**¹⁰ in the presence of *t*-BuOK in THF afforded the targeted stilbene derivative, but as an *E*-*Z* isomer mixture. The reaction of benzylic phosphonates with aromatic aldehydes under Wittig–Horner conditions is generally stereoselective,¹¹ leading to the *E* isomer only. In the present case, steric

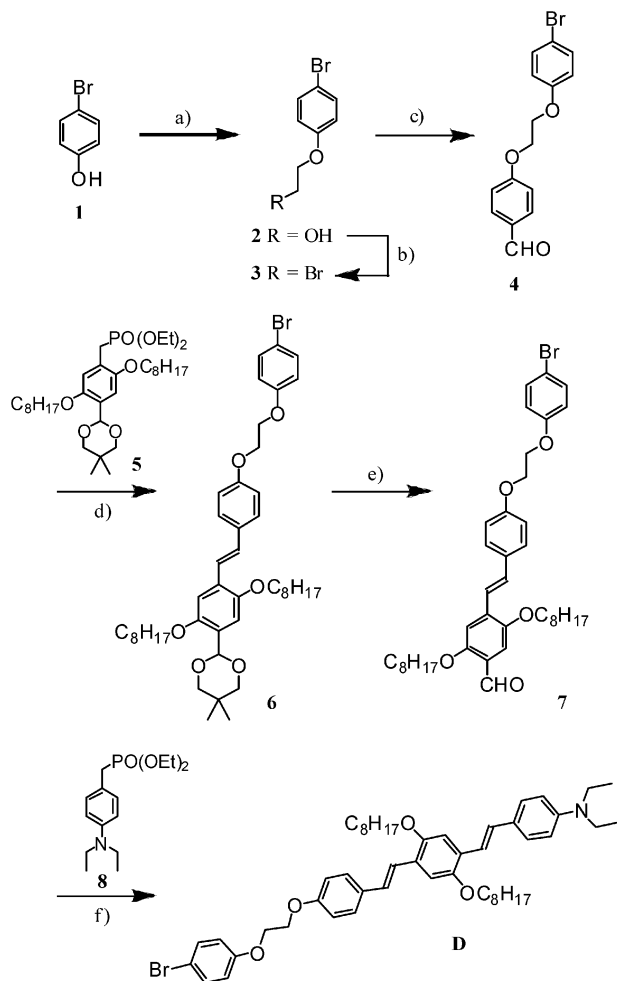
hindrance resulting from the presence of the octyloxy group in the *ortho* position of the reactive phosphonate groups may explain the lack of *E* : *Z* selectivity.¹² Isomerization to the all-*E* derivative **6** was easily achieved by treatment with a catalytic amount of iodine in refluxing toluene and compound **6** was thus obtained in 52% yield. The *E* stereochemistry of the double bond in **6** was confirmed by the coupling constant of *ca.* 16.5 Hz observed for the AX system corresponding to the signal of the vinylic protons in the 1H NMR spectrum. Treatment with trifluoroacetic acid (TFA) in CH_2Cl_2 - H_2O afforded aldehyde **7** in 80% yield. Subsequent reaction with phosphonate **8**¹³ under Wadsworth–Emmons conditions afforded the all-*E* OPV derivative **D** as attested by 1H NMR spectroscopy showing coupling constants of *ca.* 16 to 16.5 Hz for the two AX systems of the vinylic protons. The structure of **D** was further confirmed by its MALDI-TOF mass spectrum, which shows the expected molecular ion peak at *m/z* 824.95. Lithiation of compound **D** followed by quenching with formaldehyde was attempted under different experimental conditions to introduce an alcohol group on the OPV building block. However, in our hands, the targeted alcohol derivative was never obtained from **D**. Indeed, bromide **D** was found to be poorly reactive under all the attempted lithiation conditions. This prompted us to develop a new synthetic route in which the alcohol unit is introduced at an earlier stage of the synthesis (Scheme 2).

Reduction of aldehyde **4** with lithium aluminium hydride followed by reaction of the resulting **9** with triisopropylsilyl chloride (TIPSCl) afforded protected alcohol **10**. Treatment with *t*-BuLi and subsequent quenching with *N,N*-dimethylformamide (DMF) afforded aldehyde **11** in 80% yield. The preparation of the OPV backbone from compound **11** was then achieved by following the synthetic route developed for compound **D**. Reaction of **11** with phosphonate **5** under Wadsworth–Emmons conditions followed by treatment with a catalytic amount of iodine in refluxing toluene gave **12** which, after treatment with CF_3CO_2H in CH_2Cl_2 - H_2O , yielded aldehyde **13**. Subsequent reaction of **13** with phosphonate **8** in the presence of *t*-BuOK afforded OPV derivative **14** (Scheme 3). Alcohol **15** was finally obtained in 61% yield by treatment with tetra-*n*-butylammonium fluoride (TBAF) in THF at 0 °C.

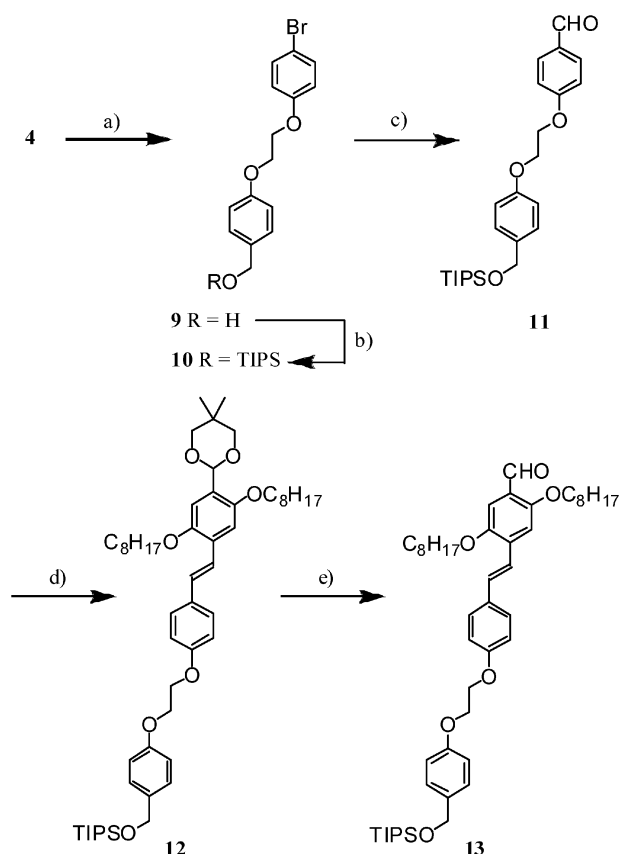
Reaction of alcohol **15** with carboxylic acid **16** under esterification conditions using *N,N'*-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) and 1-hydroxybenzotriazole (HOBt) afforded compound **F–D** in 65% yield. Both 1H - and ^{13}C -NMR spectra were in full agreement with the structure of compound **F–D**. In addition, the molecular constitution of **F–D** was further confirmed by its MALDI-TOF mass spectrum which depicted the expected molecular ion peak at *m/z* 2209.54.

Electrochemistry

The electrochemical properties of compounds **D**, **F** and **F–D** were investigated by cyclic voltammetry (CV). All the experiments were performed at room temperature in CH_2Cl_2 solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as supporting electrolyte, with a Pt wire as the working

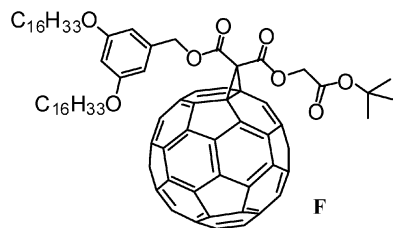


Scheme 1 Reagents and conditions: (a) 2-bromoethanol, K_2CO_3 , DMF, 80 °C (83%); (b) CBR_4 , PPh_3 , THF, 0 °C (70%); (c) 4-hydroxybenzaldehyde, K_2CO_3 , DMF, 80 °C (88%); (d) *t*-BuOK, THF, 0 °C to room temp., then I_2 , toluene, Δ (52%); (e) CF_3CO_2H , H_2O , CH_2Cl_2 , room temp. (80%); (f) *t*-BuOK, THF, 0 °C to room temp. (82%).



Scheme 2 Reagents and conditions: (a) LiAlH_4 , THF, 0 °C (84%); (b) TIPSCl, imidazole, DMF, 0 °C to room temp. (90%); (c) $t\text{-BuLi}$, THF, -78 °C, then DMF, then HCl (80%); (d) **5**, $t\text{-BuOK}$, THF, 0 °C to room temp., then I_2 , toluene, Δ (80%); (e) $\text{CF}_3\text{CO}_2\text{H}$, H_2O , CH_2Cl_2 , room temp. (70%).

electrode and a saturated calomel electrode (SCE) as a reference. Potential data for all of the compounds are collected in Table 1. Typical examples of cyclic voltammograms are shown in Fig. 1.



Compound **F** exhibits the classical behavior observed for methanofullerene derivatives.¹⁴ Whereas the first reduction observed at -0.51 V vs. SCE is always reversible, the second is irreversible at low scan rates but becomes reversible upon increasing the scan rate. The third wave gradually disappears when the second one becomes reversible, so that it probably implies reduction of the product formed after the second reduction.¹⁴ For model compound **D**, two quasi-reversible oxidation processes are observed at +0.61 and +0.85 V vs. SCE. The first one corresponds to the oxidation of the terminal tertiary amine group while the second one is most likely ascribed to an oxidation centered on the central

dialkoxyphenyl moiety.¹⁵ The cyclic voltammograms recorded for hybrid compound **F-D** shows the characteristic electrochemical features of both constitutive units, *i.e.* methanofullerene and OPV. The comparison of the $E_{1/2}$ potentials of **F-D** with the corresponding model compounds clearly shows that the three first reduction waves correspond to fullerene-centered processes, while the two oxidation processes are centered on the conjugated OPV backbone. Comparison of the redox potentials of **F-D** with those of the corresponding model compounds **F** and **D** reveals no particular electronic interactions between the two moieties.

Ground state absorption and luminescence properties

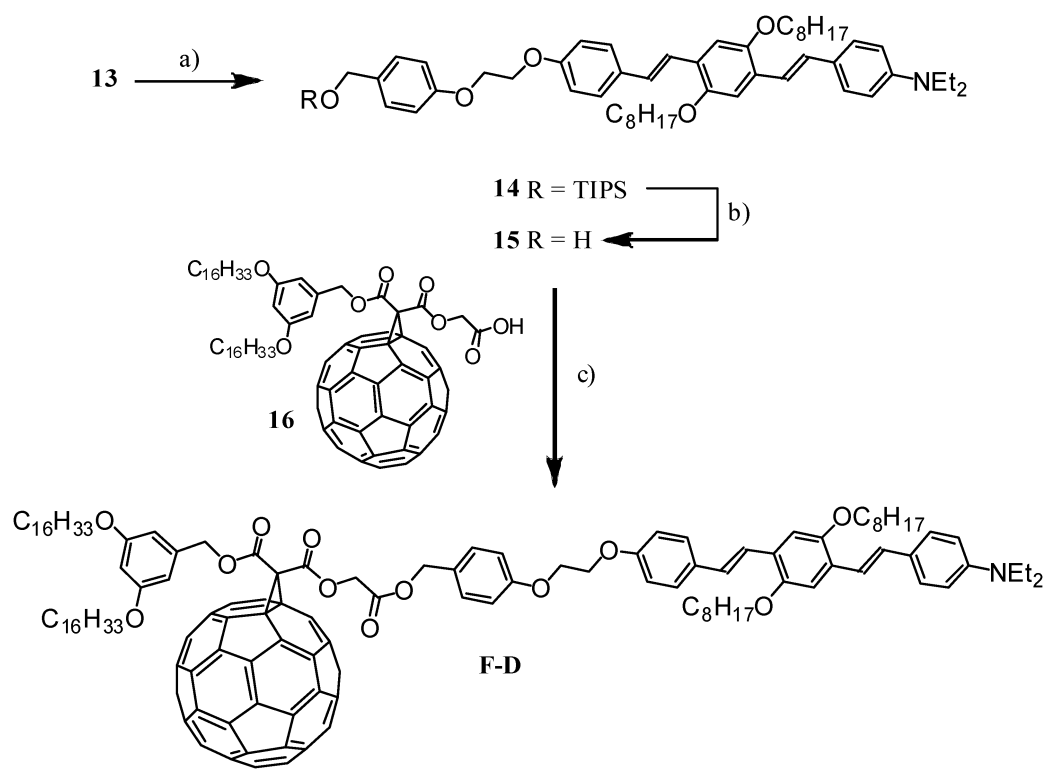
The electronic absorption spectra of **D**, **F** and **F-D** in toluene are reported in Fig. 2. For dyad **F-D**, absorption features at $\lambda < 350$ nm and $\lambda > 450$ nm are attributable to the methanofullerene moiety, whereas the wide and intense band around 425 nm is related to transitions centered on the OPV moiety. The absorption spectra of dyad **F-D** exhibit minor differences when compared with the sum of the spectra of the corresponding reference compounds, indicating negligible ground state electronic interactions in good agreement with the electrochemical data (*vide supra*).

Oligomer **D** is a quite strong fluorophore with an emission quantum yield of 0.46 and an excited state lifetime of 1.2 ns in toluene solution. This fluorescence signal, attributable to the deactivation of the lowest singlet OPV electronic level,⁷ is dramatically quenched in dyad **F-D** ($\phi = 0.031$ and $\tau < 0.5$ ns) suggesting the occurrence of OPV- C_{60} excited state interactions. As extensively discussed in the past for similar OPV- C_{60} structures,⁷ the quenching mechanism is ultrafast $^1\text{OPV}^* \rightarrow ^1\text{C}_{60}$ singlet energy transfer. Importantly, sensitization of the carbon sphere *via* the OPV moiety ($\lambda_{\text{exc}} = 450$ nm) does not result in any fullerene fluorescence even in apolar toluene.

Model compound **F** is characterized by a fluorescence band centered at 705 nm with $\tau = 1.5 \pm 0.1$ ns and $\phi = 3 \times 10^{-4}$,¹⁶ corresponding to the deactivation of the lowest-lying singlet level ($^1\text{F}^*$). In both toluene and benzonitrile, $^1\text{F}^*$ is substantially quenched in **F-D** when compared to reference **F** (Fig. 2). Moreover no singlet oxygen sensitized emission is detected in the NIR at 1270, also ruling out the population of the fullerene triplet level.¹⁷ These results can be rationalized assuming that the electronic excited states centered on the two moieties are quenched due to the presence of a low-lying charge-separated state indicated as F^--D^+ , the positive charge being located on the amine terminal residue of the OPV moiety and the negative one on the C_{60} unit (Fig. 3).

Transient absorption spectroscopy

In order to get evidence for the occurrence of photoinduced electron transfer, transient absorption investigations were carried out in benzonitrile (BN). First, bimolecular quenching experiments were accomplished, with the aim of revealing the spectral features of the involved cationic and anionic species. Transient absorption spectra in the nano- and microsecond timescale obtained with a solution of **F** (0.1 mM) in the presence of **D** (0.1 mM) in oxygen-free BN are depicted in Fig. 4. The broad absorption band peaked at 700 nm and



Scheme 3 Reagents and conditions: (a) **8**, *t*-BuOK, THF, 0 °C to room temp. (60%); (b) TBAF, THF, 0 °C (61%); (c) DCC, DMAP, HOBT, CH₂Cl₂, 0 °C to room temp. (65%).

appearing immediately after the ns-laser pulse is attributed to the fullerene triplet (³F*);¹⁶ for comparison, see the typical

long-lived triplet absorption features of **F** alone in benzonitrile (Fig. 4b). The early triplet spectral trace of **F** (700 ns) then

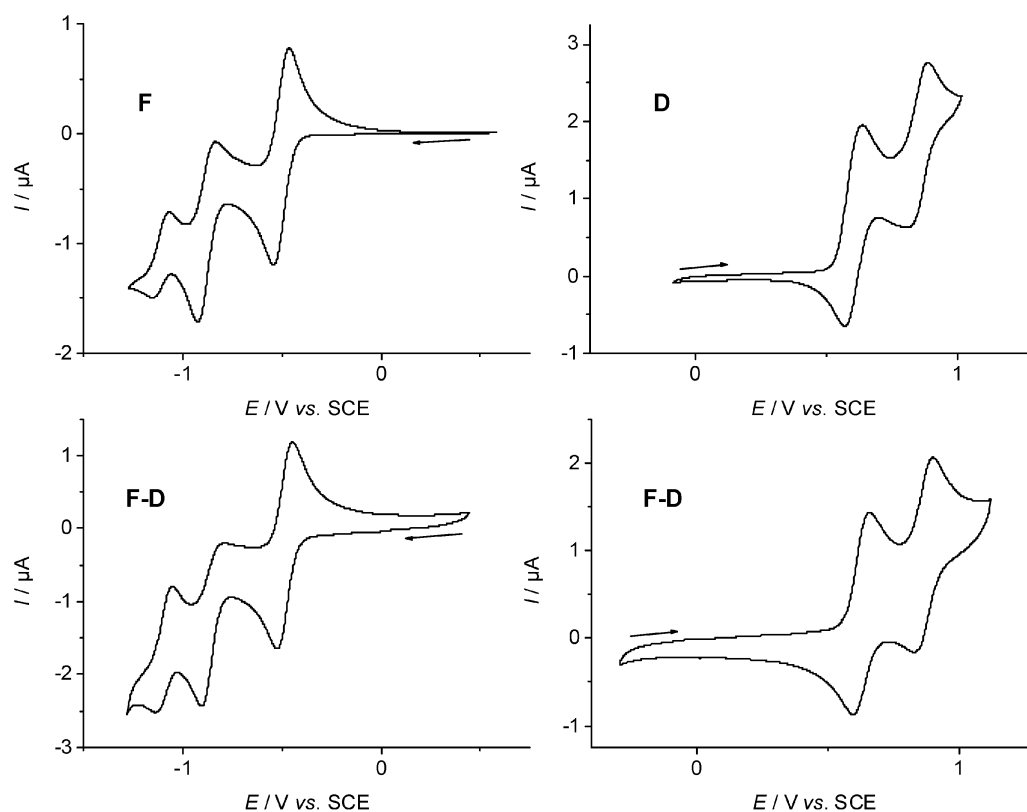


Fig. 1 Cyclic voltammograms of **F**, **D** and **F-D** on a Pt electrode at $\nu = 0.1 \text{ V s}^{-1}$ in CH₂Cl₂ + 0.1 M ⁿBu₄NBF₄.

Table 1 Electrochemical data of **F**, **D** and **F-D** determined by CV on a Pt working electrode in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M } ^n\text{Bu}_4\text{NBF}_4$ at room temperature

	Oxidation		Reduction		
	E_1^a	E_2^a	E_1^a	E_2^b	E_3^c
F	—	—	−0.51	−0.89	−1.12
D	+0.62	+0.87	—	—	—
F-D	+0.61	+0.85	−0.50	−0.87	−1.12

^a Values for $(E_{\text{pa}} + E_{\text{pc}})/2$ in V vs. SCE at a scan rate of 100 mV s^{-1} .
^b Peak potential value at a scan rate of 100 mV s^{-1} , irreversible process.
^c Waves corresponding to an electrogenerated species obtained after the second reduction step.

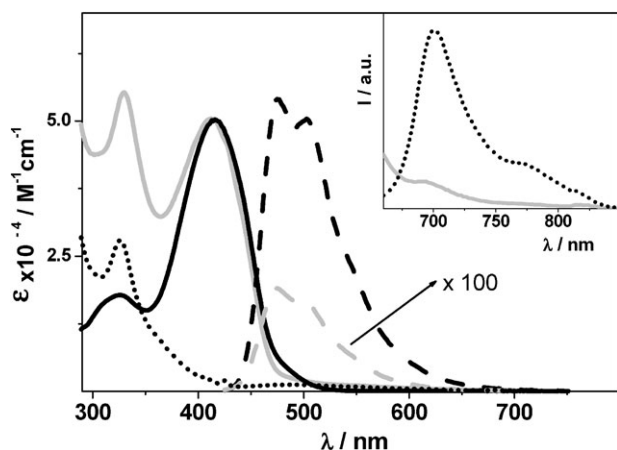


Fig. 2 Absorption spectra of **F-D** (grey) and its component chromophores **F** (dotted black) and **D** (black) at 298 K. Dashed lines: fluorescence spectra of **D** (black) and **F-D** (grey, multiplied by a factor of 100); $\lambda_{\text{exc}} = 420 \text{ nm}$, toluene. Inset: fullerene-centered fluorescence spectra: **F** (dotted black) and **F-D** (grey), $\lambda_{\text{exc}} = 550 \text{ nm}$, toluene.

disappears and a new spectral profile grows up with two broad bands in the VIS and NIR regions at $\lambda_{\text{max}} = 640$ and 1300 nm . Such bands are assigned to the radical cation of **D**¹⁸ and their rise occurs within about $15 \mu\text{s}$ after excitation (Fig. 4a, inset). By adding oxygen to the solution, where an intermolecular energy transfer from $^3\text{C}_{60}^*$ to oxygen takes place,^{19,20} the electron transfer event is suppressed and the novel spectral traces are no longer detected. The latter observation confirmed the occurrence of electron transfer from the fullerene triplet level. Despite several efforts, a detailed Stern–Volmer kinetic analysis of the bimolecular quenching process, with determination of the electron transfer yield (Φ_{et}) and rate (k_{et}),^{18,20,21} is not possible due to the substantial overlapping of the fullerene triplet spectral features with the intense radical cation bands, which prevents a reliable evaluation of the pseudo-first order decay rate constant of $^3\text{C}_{60}^*$.

Transient absorption spectra were then recorded for dyad **F-D** in deaerated benzonitrile and toluene in the ns– μs timescale. The spectral traces obtained for **F-D** are depicted in Fig. 5 and exhibit the ion pair features, *i.e.* **D** radical cation (670, 1300 nm) and **F** radical anion (1030 nm), the latter as a neat spike emerging over the intense cation background. They are compelling evidence of intramolecular electron transfer. The first order decay kinetic traces (Fig. 5, inset) are associated

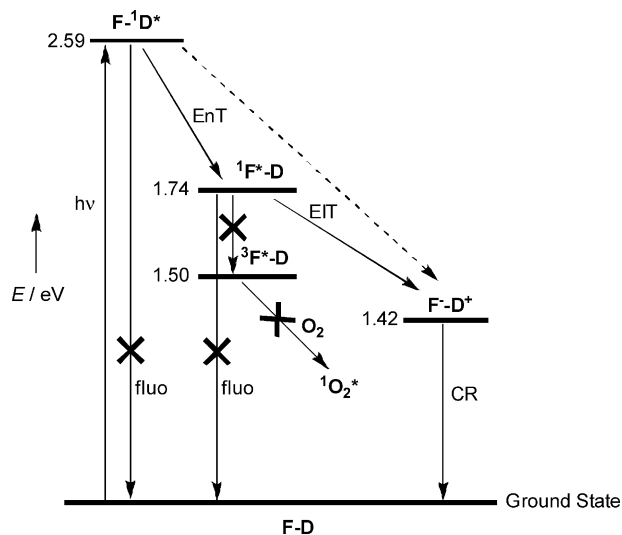


Fig. 3 Energy level diagram summarizing the photoinduced intra-molecular processes in **F-D** (EnT: energy transfer, EIT: electron transfer, CR: charge recombination). The energy of the lowest singlet excited states ($^1\text{D}^*$ and $^1\text{F}^*$) were estimated from the highest energy feature of fluorescence spectra in Fig. 2. The energy of the lowest C_{60} triplet states ($^3\text{F}^*$) was taken from earlier work.⁷ The values of the first oxidation and reduction potentials (Table 1) allow the determination of the free energy change ($-\Delta G$) of the corresponding redox process leading to the charge-separated (CS) state F-D^+ .

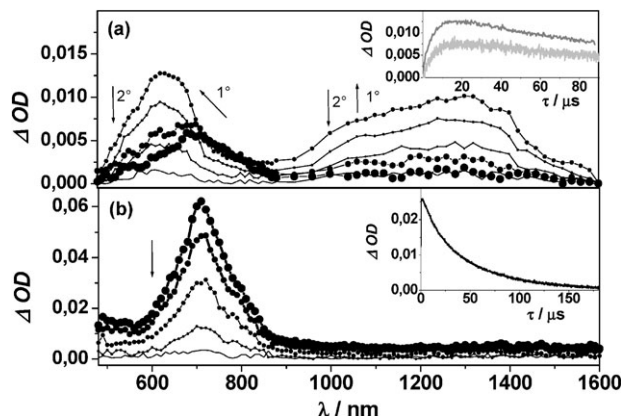


Fig. 4 (a) Transient absorption spectra of an oxygen-free benzonitrile solution containing **F** ($1 \times 10^{-4} \text{ M}$) and **D** ($1 \times 10^{-4} \text{ M}$); depicted spectral traces are at 1, 2, 11, 70, 170 and $350 \mu\text{s}$ (from bigger to smaller circles) after the laser pulse. Inset: absorbance decays at 600 nm (grey) and 1020 nm (light grey). $\lambda_{\text{exc}} = 532 \text{ nm}$; energy: 0.5 mJ per pulse. (b) Transient absorption spectra of **F** in benzonitrile; depicted spectral traces are taken between 1 and $80 \mu\text{s}$ (from bigger to smaller circles). Inset: absorbance decay at 700 nm . $\lambda_{\text{exc}} = 532 \text{ nm}$; energy: 0.5 mJ per pulse.

to the charge recombination process, yielding a lifetime of the charge-separated state of 135 and 85 ns in toluene and benzonitrile, respectively. The longer lifetime in the less polar solvent suggests a back-electron transfer process occurring in the Marcus inverted region,²² as often found in photoinduced electron transfer involving fullerene moieties^{23–26} that are characterized by an intrinsically low reorganization energy.²⁷ Notably, compared to bimolecular quenching experiments

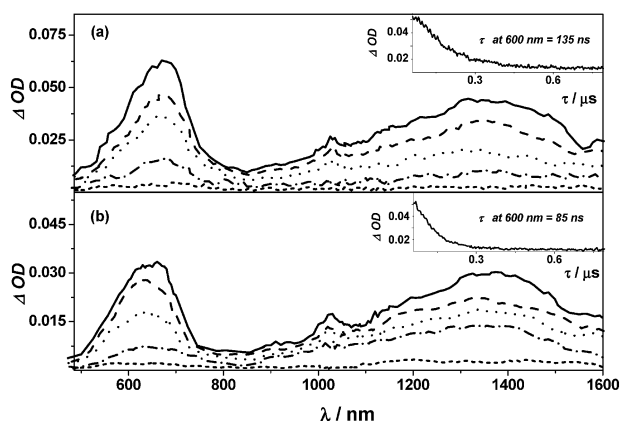


Fig. 5 Upper panel (a) transient absorption spectra of **F–D** in toluene; profiles from 0.08 μ s (black) to 1.4 μ s (black dotted line). Bottom panel (b) transient absorption spectra of **F–D** in benzonitrile; profiles from 0.05 μ s (black) to 1.6 μ s (black dotted line). Insets: absorbance decays at 600 nm for both panels; $\lambda_{\text{exc}} = 532$ nm; energy: 0.5 mJ per shot.

(*vide supra*) no triplet features are observed at the earliest time following nanosecond laser excitation, suggesting an ultrafast forward intramolecular electron transfer step from the fullerene singlet level.⁸

Conclusions

We have prepared and investigated a C_{60} -OPV hybrid system in which a dialkylamino group was attached to the OPV moiety, to serve as potential electron donor for the fullerene acceptor in photoinduced electron transfer. This process was deduced by the lack of the typical OPV and fullerene-centered fluorescence in the multicomponent array and unambiguously evidenced by means of transient absorption spectroscopy. A relatively long-lived charge-separated state was detected and the dependence of its charge recombination kinetics on the solvent polarity (135 and 85 ns in toluene and benzonitrile, respectively) suggests an inverted region regime.

Experimental

Materials and methods

All reagents were used as purchased from commercial sources without further purification. Compounds **5**,¹⁰ **8**,¹³ **16**²⁸ and **F**²⁸ were prepared according to a previously reported procedure. Solvents were dried using standard techniques prior to use. All reactions were performed in standard glassware. Evaporation was done using water aspirator and then drying *in vacuo* at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck and treated with Et_3N (1% in CH_2Cl_2) for the purification of compounds bearing NEt_2 groups. TLC: precoated glass sheets with silica gel 60 F₂₅₄ (Merck), visualization by UV light. Gel permeation chromatography was performed on Biorad, Biobeads SX-1 under the use of CH_2Cl_2 as eluent. NMR spectra were recorded on a Bruker AM 300 (300 MHz) with solvent signal as reference. MALDI-TOF-MS were obtained on a Bruker BIFLEXTM mass spectrometer. Elemental

analyses were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France).

Synthesis

Compound 2. A mixture of K_2CO_3 (21.00 g, 0.15 mol), 4-bromophenol (10.00 g, 0.06 mol), and 2-bromoethanol (5.10 mL, 0.07 mol) in DMF (100 mL) was heated at 80 °C for 72 h. The mixture was then filtered over Celite, evaporated to dryness and taken up with CH_2Cl_2 . The organic layer was washed with a saturated aqueous NaCl solution, dried (MgSO_4), filtered and evaporated. Column chromatography (SiO_2 , hexane– CH_2Cl_2 1 : 1) yielded **2** (10.00 g, 83%) as a white solid. ^1H NMR (300 MHz, CDCl_3): 7.37 (m, 2H), 6.79 (m, 2H), 3.98 (m, 4H), 2.18 (t, $J = 6$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): 157.8, 132.4, 116.4, 113.3, 69.48, 61.3.

Compound 3. CBr_4 (10.70 g, 0.03 mmol) and PPh_3 (8.39 g, 0.03 mmol) were added to a solution of **2** (5.00 g, 0.02 mmol) in anhydrous THF (200 mL) at 0 °C under argon atmosphere. The mixture was then stirred for 4 h. The solvent was removed under reduced pressure and the residue purified by column chromatography (SiO_2 , hexane– CH_2Cl_2 4 : 1) to yield **3** (3.92 g, 70%) as a white solid. ^1H NMR (300 MHz, CDCl_3): 7.40 (m, 2H), 6.79 (m, 2H), 4.28 (t, $J = 6$ Hz, 2H), 3.65 (t, $J = 6$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3): 157.2, 132.4, 116.6, 113.7, 68.1, 28.9. Anal. calcd for $\text{C}_8\text{H}_8\text{OBr}_2$: C 34.32, H 2.88%. Found: C 34.30, H 2.65%.

Compound 4. As described for **2**, with 4-hydroxybenzaldehyde (1.72 g, 14.08 mmol), **3** (4.73 g, 16.89 mmol) and K_2CO_3 (4.86 g, 35.20 mmol) in DMF (25 mL). Column chromatography (SiO_2 , hexane– CH_2Cl_2 1 : 1) yielded **4** (4.00 g, 88%) as a white solid. ^1H RMN (300 MHz, CDCl_3): 9.90 (s, 1H), 7.86 (d, $J = 9$ Hz, 2H), 7.40 (d, $J = 9$ Hz, 2H), 7.06 (d, $J = 9$ Hz, 2H), 6.84 (d, $J = 9$ Hz, 2H), 4.37 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): 190.8, 163.5, 157.6, 132.4, 132.0, 130.3, 116.5, 114.9, 113.5, 66.7, 66.5. Anal. calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3\text{Br}$: C 56.10, H 4.08%. Found: C 55.81, H 3.93%.

Compound 6. *t*-BuOK (0.22 g, 1.95 mmol) was added to a solution of **4** (0.50 g, 1.5 mmol) and **5** (1.03 g, 1.71 mmol) in anhydrous THF (30 mL) under argon atmosphere at 0 °C. The mixture was stirred for 1 h at 0 °C, then overnight at room temperature. The mixture was then filtered over Celite, evaporated to dryness and taken up with CH_2Cl_2 . The organic layer was washed with water, dried (MgSO_4), filtered and evaporated. Column chromatography (SiO_2 , hexane– CH_2Cl_2 3 : 2) gave **6** as an *E–Z* isomer mixture. The *E–Z* mixture obtained after the first chromatographic purification was directly isomerized as follows: a solution of the *E–Z* mixture and I_2 in toluene (10 mL) was refluxed for 12 h and then cooled to room temperature. The resulting toluene solution was washed with an aqueous 0.3 M $\text{Na}_2\text{S}_2\text{O}_3$ solution and water, dried (MgSO_4), filtered and evaporated. Column chromatography (SiO_2 , hexane– CH_2Cl_2 3 : 2) yielded **6** (0.60 g, 52%) as an orange solid that was used in the next step without further purifications. ^1H NMR (300 MHz, CDCl_3): 7.46 (d, $J = 9$ Hz, 2H), 7.39 (d, $J = 9$ Hz, 2H), 7.34 (d, $J = 16.5$ Hz, 1H), 7.19 (s, 1H), 7.08 (s, 1H), 7.05 (d, $J = 16.5$ Hz, 1H), 6.93 (d, $J = 9$ Hz, 2H), 6.84 (d, $J = 9$ Hz, 2H), 5.75 (s, 1H), 4.31 (m, 4H),

4.02 (t, $J = 6$ Hz, 4H), 3.72 (AB, $J = 11$ Hz, 4H), 1.82 (m, 4H), 1.32 (m, 23H), 0.89 (m, 6H), 0.81 (s, 3H).

Compound 7. TFA (3 mL) was added dropwise to a solution of **6** (0.56 g, 0.73 mmol) in $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$ 1 : 1 (12 mL). The mixture was then stirred for 2 h, washed with H_2O (until pH was near neutrality), dried (MgSO_4), filtered and evaporated. Column chromatography (SiO_2 , hexane- CH_2Cl_2 3 : 2) yielded **7** (0.40 g, 80%) as an orange solid. ^1H NMR (300 MHz, CDCl_3): 10.45 (s, 1H), 7.50 (d, $J = 9$ Hz, 2H), 7.40 (d, $J = 9$ Hz, 2H), 7.36 (d, $J = 16.5$ Hz, 1H), 7.32 (s, 1H), 7.20 (d, $J = 16.5$ Hz, 1H), 7.15 (s, 1H), 6.95 (d, $J = 9$ Hz, 2H), 6.84 (d, $J = 9$ Hz, 2H), 4.32 (m, 4H), 4.10 (t, $J = 6$ Hz, 2H), 4.02 (t, $J = 6$ Hz, 2H), 1.85 (m, 4H), 1.30 (m, 20H), 0.88 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): 189.1, 158.7, 157.8, 156.3, 150.6, 134.7, 132.4, 131.8, 130.6, 128.3, 124.0, 121.1, 116.5, 114.9, 110.3, 110.1, 69.3, 69.1, 66.8, 66.5, 31.8, 29.4, 29.35, 29.3, 26.2, 26.15, 22.7, 14.1.

Compound D. *t*-BuOK (93 mg, 0.83 mmol) was added to a solution of **7** (0.45 g, 0.66 mmol) and **8** (0.30 g, 0.99 mmol) in anhydrous THF (13 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred for 1 h at 0 °C, then for 2 h at room temperature. The mixture was then filtered over Celite, evaporated and taken up with CH_2Cl_2 . The organic layer was washed with water, dried (MgSO_4), filtered and evaporated. Column chromatography (SiO_2 , CH_2Cl_2) yielded **D** (0.45 g, 82%) as an orange solid. ^1H NMR (300 MHz, CDCl_3): 7.47 (d, $J = 9$ Hz, 2H), 7.42 (d, $J = 9$ Hz, 2H), 7.40 (d, $J = 9$ Hz, 2H), 7.33 (s, 1H), 7.27 (d, $J = 16.5$ Hz, 1H), 7.14 (d, $J = 16$ Hz, 1H), 7.10 (s, 1H), 7.06 (d, $J = 16$ Hz, 1H), 7.05 (d, $J = 16.5$ Hz, 1H), 6.94 (d, $J = 9$ Hz, 2H), 6.85 (d, $J = 9$ Hz, 2H), 6.68 (d, $J = 9$ Hz, 2H), 4.31 (m, 4H), 4.04 (2t, $J = 6$ Hz, 4H), 3.39 (q, $J = 7$ Hz, 4H), 1.87 (m, 4H), 1.31 (m, 20H), 1.19 (t, $J = 7$ Hz, 6H), 0.89 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): 158.0, 157.8, 151.1, 150.7, 147.3, 132.3, 131.6, 128.9, 127.9, 127.7, 127.5, 126.0, 125.5, 121.9, 118.5, 116.6, 114.9, 113.3, 111.7, 110.8, 110.1, 69.8, 69.6, 66.8, 66.5, 44.4, 31.9, 31.85, 29.65, 29.6, 29.5, 29.45, 29.4, 26.3, 22.75, 22.7, 14.1, 12.7. Anal. calcd for $\text{C}_{50}\text{H}_{66}\text{O}_4\text{BrN}$: C 72.80, H 8.06, N 1.70%. Found: C 73.04, H 8.15, N 1.48%. MS-MALDI: calcd for $\text{C}_{50}\text{H}_{66}\text{O}_4\text{BrN}$ 824.96. Found: 824.95 $[\text{M}]^+$.

Compound 9. A 1 M LiAlH_4 solution in THF (10 mL, 10 mmol) was added dropwise to a solution of **4** (2.50 g, 7.78 mmol) in anhydrous THF (150 mL) at 0 °C. The mixture was stirred for 2 h. Precipitate of the aluminium salts was obtained upon addition of methanol and H_2O . The mixture was then filtered over Celite and evaporated to dryness. The residue was recrystallized from hexane to yield **9** (2.10 g, 84%). ^1H NMR (300 MHz, CDCl_3): 7.39 (d, $J = 9$ Hz, 2H), 7.30 (d, $J = 9$ Hz, 2H), 6.94 (d, $J = 9$ Hz, 2H), 6.84 (d, $J = 9$ Hz, 2H), 4.63 (s, 2H), 4.30 (s, 4H). ^{13}C NMR (75 MHz, CDCl_3): 158.2, 157.8, 133.6, 133.3, 128.7, 116.5, 114.8, 113.4, 66.6, 66.5, 65.0. Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{Br}$: C 55.75, H 4.68%. Found: C 55.84, H 4.71%.

Compound 10. TIPSCl (1.20 mL, 4.64 mmol) and imidazole (0.76 g, 11.14 mmol) were added to a solution of **9** (1.50 g, 4.64 mmol) in DMF (12 mL) at 0 °C under argon. The reaction

mixture was stirred overnight at room temperature. Water (100 mL) was then added to the reaction mixture and it was extracted with ether (3×20 mL). The organic layer was washed with water, dried (MgSO_4), filtered and evaporated. The residue was recrystallized from hexane to yield **10** (2.00 g, 90%). ^1H NMR (300 MHz, CDCl_3): 7.38 (d, $J = 9$ Hz, 2H), 7.28 (d, $J = 9$ Hz, 2H), 6.92 (d, $J = 9$ Hz, 2H), 6.85 (d, $J = 9$ Hz, 2H), 4.73 (s, 2H), 4.31 (s, 4H), 1.11 (m, 21H). ^{13}C NMR (75 MHz, CDCl_3): 157.5, 157.2, 134.5, 132.3, 127.2, 116.5, 114.7, 113.3, 66.6, 66.5, 64.7, 18.1, 12.1. Anal. calcd for $\text{C}_{24}\text{H}_{35}\text{O}_3\text{BrSi}$: C 60.11, H 7.36%. Found: C 60.03, H 7.60%.

Compound 11. A 1.7 M solution of *t*-BuLi in THF (2.40 mL, 4.06 mmol) was added dropwise to a solution of **10** (0.97 g, 2.03 mmol) in anhydrous THF (10 mL) at -78 °C under argon atmosphere. After 3 h at -78 °C, dry DMF (0.24 mL, 3.05 mmol) was added and the resulting mixture was allowed to warm to room temperature. The mixture was stirred for 2 h, then an aqueous 1 M HCl solution was added. The solvent was removed under reduced pressure and the residue taken up with CH_2Cl_2 . The organic layer was washed with water, dried (MgSO_4), filtered and evaporated. Column chromatography (SiO_2 , hexane- CH_2Cl_2 2 : 1) yielded **11** (0.69 g, 80%) as a white solid. ^1H NMR (300 MHz, CDCl_3): 9.90 (s, 1H), 7.85 (d, $J = 9$ Hz, 2H), 7.29 (d, $J = 9$ Hz, 2H), 7.06 (d, $J = 9$ Hz, 2H), 6.92 (d, $J = 9$ Hz, 2H), 4.78 (s, 2H), 4.38 (m, 4H), 1.11 (m, 21H). ^{13}C NMR (75 MHz, CDCl_3): 190.8, 163.7, 157.4, 134.6, 131.9, 130.2, 127.1, 114.9, 114.4, 66.9, 66.3, 64.6, 18.1, 12.0. Anal. calcd for $\text{C}_{25}\text{H}_{36}\text{O}_4\text{Si}$: C 70.05, H 8.47%. Found: C 69.89, H 8.33%.

Compound 12. As described for **6**, with **11** (0.44 g, 1.01 mmol), **5** (0.73 g, 1.21 mmol) and *t*-BuOK (0.15 g, 1.22 mmol) in anhydrous THF (20 mL). Column chromatography (SiO_2 , hexane- CH_2Cl_2 1 : 1) yielded **12** (0.69 g, 80%) as an orange glassy product. ^1H NMR (300 MHz, CDCl_3): 7.46 (d, $J = 9$ Hz, 2H), 7.39 (d, $J = 9$ Hz, 2H), 7.34 (d, $J = 16.5$ Hz, 1H), 7.19 (s, 1H), 7.08 (s, 1H), 7.05 (d, $J = 16.5$ Hz, 1H), 6.93 (d, $J = 8$ Hz, 2H), 6.92 (d, $J = 8$ Hz, 2H), 5.75 (s, 1H), 4.77 (s, 2H), 4.31 (s, 4H), 4.02 (2t, $J = 6$ Hz, 4H), 3.72 (AB, $J = 11$ Hz, 4H), 1.82 (m, 4H), 1.32 (m, 23H), 1.1 (m, 21H), 0.89 (t, $J = 7$ Hz, 6H), 0.88 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 158.2, 157.6, 151.0, 150.3, 141.1, 134.4, 130.3, 128.5, 128.1, 127.7, 127.2, 126.9, 121.8, 114.9, 114.5, 114.2, 111.5, 110.5, 91.1, 69.6, 69.4, 69.2, 66.6, 64.7, 31.85, 31.8, 30.3, 29.7, 29.5, 29.45, 29.4, 29.35, 29.3, 26.3, 26.1, 23.2, 22.75, 22.7, 21.9, 18.1, 14.1, 12.1.

Compound 13. As described for **7**, with **12** (0.40 g, 0.46 mmol) and TFA (3 mL) in $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$ 1 : 1 (10 mL). Column chromatography (SiO_2 , hexane- CH_2Cl_2 1 : 1) yielded **13** (0.25 g, 70%) as a red glassy product. ^1H NMR (300 MHz, CDCl_3): 10.47 (s, 1H), 7.46 (d, $J = 9$ Hz, 2H), 7.33 (d, $J = 16.5$ Hz, 1H), 7.31 (d, $J = 9$ Hz, 2H), 7.18 (s, 1H), 7.05 (d, $J = 16.5$ Hz, 1H), 7.01 (s, 1H), 6.99 (d, $J = 8$ Hz, 2H), 6.95 (d, $J = 8$ Hz, 2H), 4.80 (s, 2H), 4.37 (s, 4H), 4.00 (2t, $J = 6$ Hz, 4H), 1.85 (m, 4H), 1.39–1.25 (m, 20H), 1.10 (m, 21H), 0.89 (t, $J = 7$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3): 189.1, 158.9, 157.5, 156.3, 150.6, 134.7, 134.4, 131.8, 130.4, 128.2, 127.2, 123.9, 121.0, 115.0, 114.4, 110.3, 110.1, 69.2, 69.1,

66.7, 66.6, 64.7, 31.8, 29.7, 29.35, 29.3, 29.25, 26.2, 26.1, 22.7, 18.1, 17.7, 14.1, 12.1.

Compound 14. As described for **D**, with **13** (0.30 g, 0.38 mmol), **8** (0.24 g, 0.72 mmol) and *t*-BuOK (56 mg, 0.45 mmol) in anhydrous THF (20 mL). Column chromatography (SiO₂, hexane–CH₂Cl₂ 1 : 1) yielded **14** (213 mg, 60%) as an orange glassy product. ¹H NMR (300 MHz, CDCl₃): 7.49 (d, *J* = 8 Hz, 2H), 7.40 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 17 Hz, 1H), 7.32 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 17 Hz, 1H), 7.12 (s, 1H), 7.10 (s, 1H), 7.06 (d, *J* = 17 Hz, 1H), 6.98 (d, *J* = 17 Hz, 1H), 6.97 (d, *J* = 8 Hz, 2H), 6.96 (d, *J* = 8 Hz, 2H), 6.70 (d, *J* = 8 Hz, 2H), 4.65 (s, 2H), 4.36 (s, 4H), 4.05 (2t, *J* = 7 Hz, 4H), 3.41 (q, *J* = 7 Hz, 4H), 1.87 (m, 4H), 1.39–1.25 (m, 20H), 1.20 (t, *J* = 7 Hz, 6H), 1.10 (m, 21H), 0.88 (t, *J* = 7 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): 158.1, 157.6, 134.4, 127.8, 127.6, 127.1, 121.8, 118.5, 118.5, 115.9, 114.4, 111.7, 110.1, 69.8, 69.6, 66.65, 66.6, 64.7, 44.4, 31.9, 31.85, 31.8, 29.7, 29.6, 29.55, 29.5, 29.45, 29.35, 29.3, 29.25, 26.3, 22.7, 18.1, 14.1, 12.7, 12.1.

Compound 15. A 1 M solution of TBAF in THF (0.40 mL, 0.40 mmol) was added dropwise to a solution of **14** (168 mg, 0.18 mmol) in anhydrous THF (10 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred for 2 h and water was added. The solvent was removed under reduced pressure and the residue taken up with CH₂Cl₂. The organic layer was washed with water, dried (MgSO₄), filtered and evaporated. Column chromatography (SiO₂, hexane–CH₂Cl₂ 7 : 3) yielded **15** (85 mg, 61%) as an orange glassy product. ¹H NMR (300 MHz, CDCl₃): 7.49 (d, *J* = 8 Hz, 2H), 7.40 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 17 Hz, 1H), 7.32 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 17 Hz, 1H), 7.12 (s, 1H), 7.10 (s, 1H), 7.06 (d, *J* = 17 Hz, 1H), 6.98 (d, *J* = 17 Hz, 1H), 6.97 (d, *J* = 8 Hz, 2H), 6.96 (d, *J* = 8 Hz, 2H), 6.70 (d, *J* = 8 Hz, 2H), 4.65 (s, 2H), 4.36 (s, 4H), 4.05 (m, 4H), 3.41 (q, *J* = 7 Hz, 4H), 1.88 (m, 4H), 1.39–1.25 (m, 20H), 1.20 (t, *J* = 7 Hz, 6H), 0.88 (t, *J* = 7 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): 161.0, 158.3, 158.0, 151.1, 150.7, 140.2, 133.6, 131.5, 128.8, 128.7, 128.6, 127.8, 127.7, 127.65, 127.6, 126.0, 121.8, 114.9, 114.8, 111.9, 110.7, 110.1, 70.1, 69.8, 69.6, 67.1, 66.6, 66.5, 65.0, 55.9, 45.6, 44.6, 44.5, 42.3, 38.2, 31.9, 31.8, 29.6, 29.55, 29.45, 29.3, 29.3, 26.3, 22.75, 22.7, 14.1, 12.6.

Compound F–D. DCC (20 mg, 0.10 mmol) was added to a solution of **15** (50 mg, 0.07 mmol), **16** (143 mg, 0.10 mmol) and DMAP (4.80 mg, 0.04 mmol) in CH₂Cl₂ (50 mL) at 0 °C. The solution was stirred for 1 h at 0 °C and after that period a catalytic amount of HOBt was added. The mixture was then stirred for 2 h at 0 °C, then for 12 h at room temperature. The mixture was then filtered and evaporated. Column chromatography (SiO₂, hexane–CH₂Cl₂ 7 : 3) yielded **F–D** (100 mg, 65%) as a brown glassy product. ¹H NMR (300 MHz, CDCl₃): 7.46 (d, *J* = 8 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 7.23–7.34 (m, 4H), 7.10 (s, 1H), 7.08–7.01 (m, 3H), 6.93 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 8 Hz, 2H), 6.66 (d, *J* = 8 Hz, 2H), 6.59 (d, *J* = 2 Hz, 2H), 6.39 (t, *J* = 2 Hz, 1H), 5.42 (s, 2H), 5.20 (s, 2H), 4.97 (s, 2H), 4.32 (s, 4H), 4.03 (2t, *J* = 7 Hz, 4H), 3.86 (t, *J* = 7 Hz, 4H), 3.38 (q, *J* = 7 Hz, 4H), 1.86 (m, 4H), 1.73 (m, 4H), 1.39–1.25 (m, 72H), 1.18 (t, *J* = 7 Hz, 6H),

0.88 (t, *J* = 7 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): 166.4, 163.0, 160.5, 158.9, 145.25, 145.2, 145.15, 145.1, 145.0, 144.9, 144.7, 144.6, 144.5, 144.45, 143.9, 143.8, 143.0, 142.9, 142.2, 141.9, 141.8, 140.9, 140.85, 139.8, 138.4, 136.6, 130.4, 127.95, 127.85, 127.8, 127.8, 127.75, 127.7, 127.65, 127.6, 127.55, 127.4, 114.9, 110.1, 107.4, 101.7, 71.2, 69.8, 69.6, 69.1, 68.2, 67.3, 66.6, 66.5, 66.45, 62.7, 31.95, 31.9, 31.85, 29.7, 26.3, 26.3, 26.1, 22.7, 14.1. Anal. calcd for C₁₅₅H₁₄₁NO₁₂: C 84.25, H 6.43, N 0.63%. Found: C 84.22, H 6.60, N 0.75%. MS-MALDI: calcd for C₁₅₅H₁₄₁NO₁₂ 2209.82. Found: 2209.54 [M]⁺.

Electrochemistry

The cyclic voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of *ca.* 1 cm² apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte [*n*Bu₄N][BF₄] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled over CaH₂ prior to use. The solutions used during the electrochemical studies were typically 10^{−3} M in compound and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, Fc⁺/Fc is observed at +0.54 ± 0.01 V vs. SCE.

Photophysics

The photophysical investigations were carried out in benzonitrile and toluene (Carlo Erba, spectrofluorimetric grade). Absorption spectra were recorded with a Perkin-Elmer λ40 spectrophotometer. Emission spectra were obtained with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm) or a Hamamatsu R5509-72 supercooled photomultiplier tube (193 K, 800–1700 nm range). Emission quantum yields were determined according to the approach described by Demas and Crosby²⁹ using quinine sulfate in 1 N H₂SO₄ (Φ = 0.546)³⁰ as standard. Emission lifetimes were determined with the time correlated single photon counting technique using an Edinburgh FLS920 spectrometer equipped with a laser diode head as excitation source (1 MHz repetition rate, λ_{exc} = 407 or 635 nm, 200 ps time resolution upon deconvolution) and an Hamamatsu R928 PMT as detector. Transient absorption spectra in the nanosecond–microsecond time domain were obtained by using the nanosecond flash photolysis apparatus described previously.³¹ Experimental uncertainties are estimated to be 8% for lifetime determinations, 20% for emission quantum yields, 10% for relative emission intensities in the NIR, 1 nm and 5 nm for absorption and emission peaks, respectively.

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