DOI: 10.1002/asia.201000681

Synthesis, Photophysical, and Two-Photon Absorption Properties of Elongated Phosphane Oxide and Sulfide Derivatives

Valérie Alain-Rizzo,[a] Delphine Drouin-Kucma,[b] Cédric Rouxel,[b] Issa Samb,[c] Jérémy Bell,[a] Patrick Y. Toullec,[c] Véronique Michelet,*[c] Isabelle Leray,*[a] and Mireille Blanchard-Desce*[b]

Abstract: A series of rod-shaped and related three-branched push–pull derivatives containing phosphane oxide or phosphane sulfide (PO or PS)—as an electron-withdrawing group conjugated to electron-donating groups, such as amino or ether groups, with a conjugated rod consisting of arylene–vinylene or arylene–ethynylene building blocks—were prepared. These compounds were efficiently synthesized by a Grignard reaction followed by Sonogashira coupling. Their photophysical properties including absorption, emission, time-resolved fluorescence, and two-photon absorption (TPA) were investigated with special attention to structure–property relationships. These fluorophores show high fluorescence quantum yields and solvent-dependent experiments reveal that efficient intramolecular charge transfer occurs upon excitation, thereby leading to highly polar excited states, the polarity of which can be significantly enhanced by playing on the end groups and conjugated linker. Rod-shaped and related three-branched systems show similar fluorescence properties in agreement with excitation localization on one of the push–pull branches. By using stronger electron donors or replacing the arylene–ethynylene linkers with an arylene–vinylene one induces significant redshifts of both the low-energy one-photon absorption and TPA bands. Interestingly, a major enhancement in TPA responses is observed, whereas OPA intensities are only weakly affected. Similarly, phosphane oxide derivatives show similar OPA responses than the corresponding sulfides but their TPA responses are significantly larger. Finally, the electronic coupling between dipolar branches promoted by common PO or PS acceptor moieties induces either slight enhancement of the TPA responses or broadening of the TPA band in the near infrared (NIR) region. Such behavior markedly contrasts with triphenylamine-core-mediated coupling, which gives evidence for the different types of interactions between branches.

Keywords: charge transfer · fluorescence · phosphanes · solvatochromism · two-photon absorption

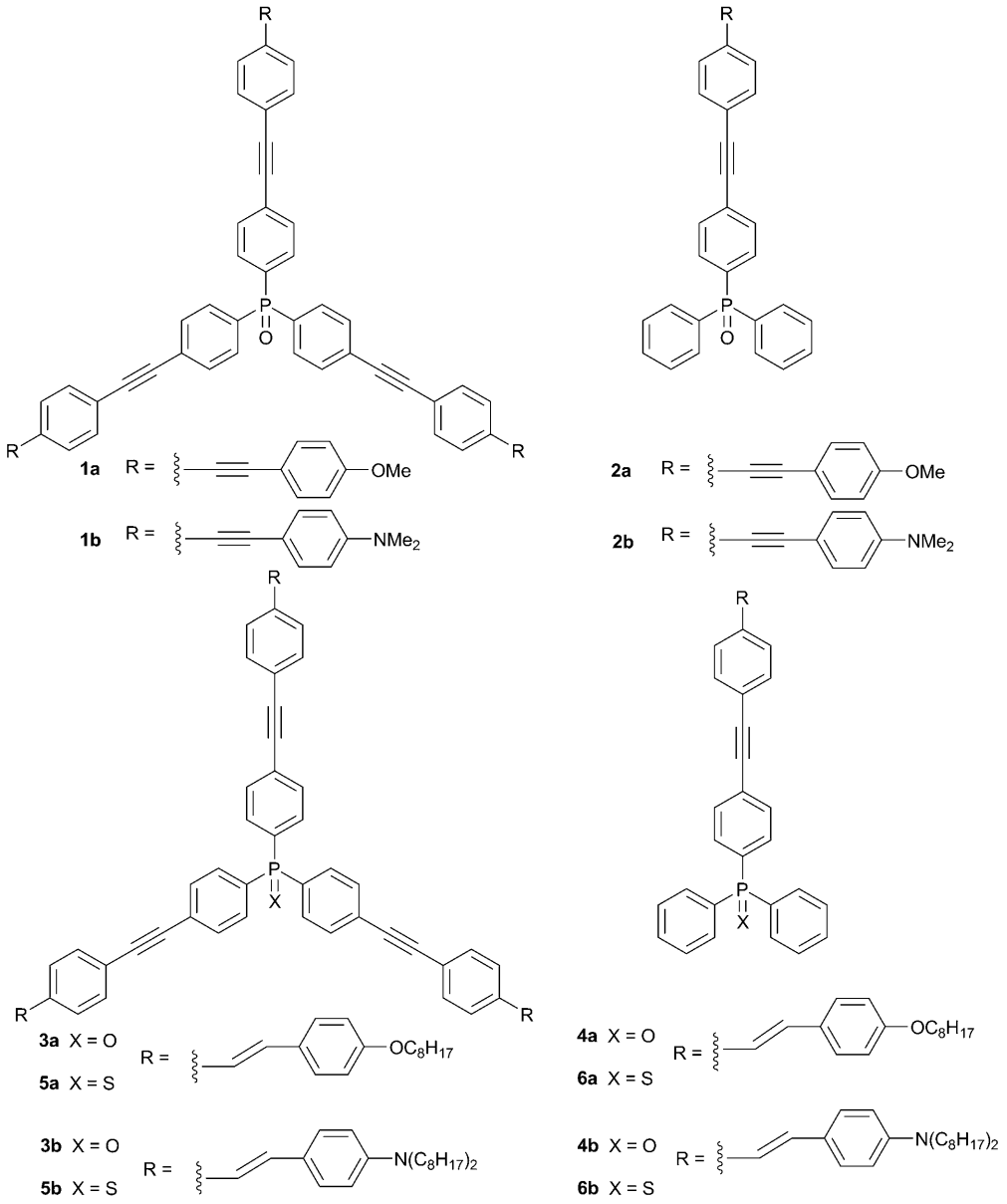
Introduction

Over the past few years significant research has been directed toward the development of new fluorescent molecules for potential applications in biology[1] or for the environment with the development of sensors.[2] In the course of our recent ongoing program toward novel fluorophores, we have recently prepared and evaluated the photophysical

[a] Dr. V. Alain-Rizzo, J. Bell, Dr. I. Leray
PPSM, ENS de Cachan, CNRS (UMR 8531)
UniverSud Paris, 61 avenue du Président Wilson
94230 Cachan (France)
Fax: (+33) 147402454
E-mail: isabelle.leray@ppsm.ens-cachan.fr

[b] D. Drouin-Kucma, C. Rouxel, Dr. M. Blanchard-Desce
Université de Rennes 1, CNRS
Chimie et Photonique Moléculaires (UMR6510)
Campus de Beaulieu Case 1003
35042, Rennes Cedex (France)
Fax: (+33) 223236955
E-mail: mireille.blanchard-desce@univ-rennes1.fr

[c] Dr. I. Samb, Dr. P. Y. Toullec, Dr. V. Michelet
Ecole Nationale Supérieure de Chimie de Paris
Chimie ParisTech, Laboratoire Charles Friedel
UMR CNRS 7223, 11 rue P. et M. Curie
75231 Paris Cedex 05 (France)
Fax: (+33) 144071062
E-mail: veronique-michelet@chimie-paristech.fr



properties of novel molecules **1**–**2**, bearing a phosphane oxide (PO) as an acceptor group and a methoxy or a dimethylamino group as the donor moiety.[3–7] These systems exhibit high fluorescence quantum yields and the excitation induces very efficient charge redistribution in the molecules, typical of an intramolecular charge-transfer transition (ICT). We also demonstrated that the electronic properties of **1**–**2** are strongly affected by the nature of the donor, the length, and the nature of the conjugated linker between the core acceptor and the peripheral donors. The photophysical properties of the star-shaped fluorophores (**1a**–**b**) and rod-shaped (**2a**–**b**) fluorophores were found to be similar, which indicated that emission originates from a single branch for all star-shaped derivatives. These branched derivatives—in which dipolar ICT branches are connected by a common acceptor core—are thus interesting model compounds for investigating the ability of the triphenylphosphane oxide (TPPO) moiety to promote coupling between dipolar branches, thereby leading to modification of (linear or nonlinear) absorption properties. Whereas the donating triphenylamine moiety is known as an efficient electron-donating coupling unit promoting coherent coupling between branches (both in octupolar derivatives[8–11] and in branched derivatives),[12] little is known about using TPPO as an electron-withdrawing coupling unit possibly promoting excitonic coupling.

The nature and strength of the electronic coupling promoted by a (electron-donating or -withdrawing) coupling unit can be evaluated by investigating the photophysical and two-photon absorption (TPA) properties of derivatives built from dipolar branches connected by such moieties. Such methodology has already proven useful in the case of the triphenylamine core unit, which was shown to be a potent coupling unit[13,14] and 1,3,5-triphenylbenzene (shown to be a

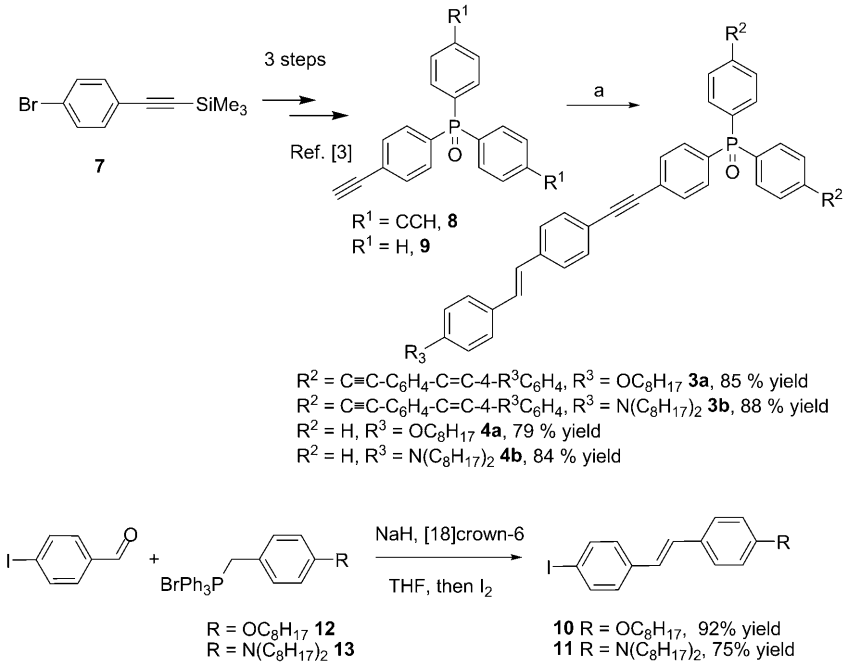
poor coupling unit).[14,15] Hence we have investigated the TPA properties of the previously described compounds (**1**–**2**) as well as of the newly synthesized derivatives **3**–**4** for which the conjugated path has been modified by the replacement of one phenylene–ethynylene (PE) building block with a phenylene–vinylene one (PV) to favor a red-shift of both TPA and one-photon absorption (OPA) spectra and enhance TPA responses.[15,16] Following this aim, we have also been interested in investigating the behavior of phosphane sulfide (PS) analogues (**5a**, **5b**, **6a**, and **6b**), anticipating that the triphenylphosphane sulfide (TPPS) moiety would affect coupling and influence both fluorescence and TPA properties. Having no precedent and no data for such derivatives, we wish therefore to describe therein our study concerning the synthesis, photophysical, and TPA properties of these new derivatives.

Results and Discussion

The preparation of **1**–**2** was realized according to previous methodologies.[3,5] The synthesis of **3**–**6** has been conducted as described in Schemes 1 and 2. By starting from the commercially available 4-bromotrimethylsilyl phenylacetylene (**7**), the phosphorylation by using the Grignard derivative in the presence of trichlorophosphane or chlorodiphenylphosphane followed by the oxidation of the phosphorus atom and the desilylation step under basic conditions afforded the key intermediates **8** and **9** in 44 and 60% overall yield, respectively (Scheme 1).[3] The introduction of one or three phenyl-vinylene arms was envisaged through the iodostyrene intermediates **10** and **11**. They were easily prepared by starting from 4-iodobenzaldehyde and the phosphonium salt bearing either an *O*-octyl or *N*-(octyl)$_2$ group.[17] The Wittig reaction employed compounds **12** and **13**, respectively (using solid-liquid phase-transfer conditions);[18] this afforded the desired iodostyrene derivatives **10** and **11** in 92% and 75% isolated yield, respectively.[16,19] It should be noted that the treatment of the crude reaction mixture with catalytic iodine under natural light led to complete *E* stereochemistry of the alkene function. The Sonogashira cross-couplings[20] were then performed either on trialkyne **8** or on monoalkyne **9**. The star-shaped phosphane oxides **3a** and **3b** were obtained in 85 and 88% yield, respectively. The mono-substituted analogues **4a** and **4b** were isolated in good yield.

The syntheses of the phosphane sulfides **5**–**6** followed the same strategy (Scheme 2). Starting from the same precursor **7**, the phosphorylation using the Grignard derivative in the presence of trichlorophosphane or chlorodiphenylphosphane was this time followed by treatment with elemental sulfur and the desilylation step under basic conditions afforded the key intermediates **8′** and **9′** in 42 and 52% overall yield, respectively (Scheme 2).[3]

The Sonogashira cross-couplings between the thiophosphano products **8′** (**9′**, respectively) and the iodostyrene derivatives **10** or **11** were performed in the presence of palladium catalyst (5 mol%) and copper iodide (15 mol%) in toluene at 60°C; this led to the desired phosphane sulfides **5a**–**b** (**6a**–**b**, respectively) in 71 and 63% (70 and 65%, respectively) isolated yield.

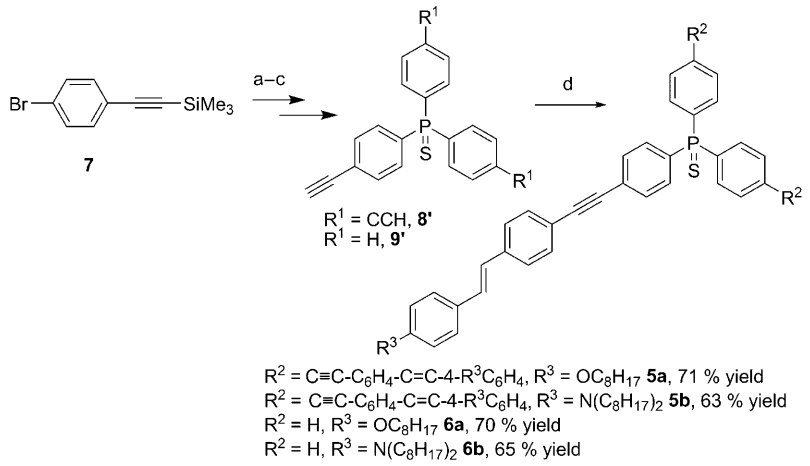


Scheme 1. Syntheses of phosphane oxides **3** and **4** and iodostyrene intermediates **10** and **11**: a) **10** or **11**, [$PdCl_2(PPh_3)_2$] (5 mol%), CuI (15 mol%), *i*Pr_2NH, toluene, 50°C, 20 h; b) NaH, [18]crown-6, THF, 20°C, then I_2 (3 mol%), CH_2Cl_2, RT, *hv*.

Photophysical Properties

The absorption and emission spectra of the newly synthesized phosphane oxide compounds are displayed in Figures 1a and b. The absorption and emission data of all compounds (including phosphane sulfide derivatives **5**–**6**) together with those previously reported for the PO derivatives containing a phenyl–ethynylene bridge are collected in Table 1. As previously observed for compounds containing diphenylene–ethynylene bridges (PE_2) as the conjugated path between the donating peripheral groups (compounds **1**–**2**) and the TPPO moiety, the PO as well as PS compounds containing phenylene–ethynylene phenylene–vinylene bridges (PE–PV; compounds **3**–**6**) show an in-

CHEMISTRY
AN ASIAN JOURNAL



Scheme 2. Syntheses of phosphane sulfides **5** and **6**: a) Mg/THF , 55 °C then $PSCl_3$ or $ClPPh_2$; b) S_8/toluene, 95 °C; c) K_2CO_3, MeOH/CH_2Cl_2 (2:1), **8′** (42 %, over 3 steps) and **9′** (52 %, over 3 steps); d) **10** or **11**, [$PdCl_2(PPh_3)_2$] (5 mol %), CuI (15 mol %), iPr_2NH, toluene, 60 °C, 3 h.

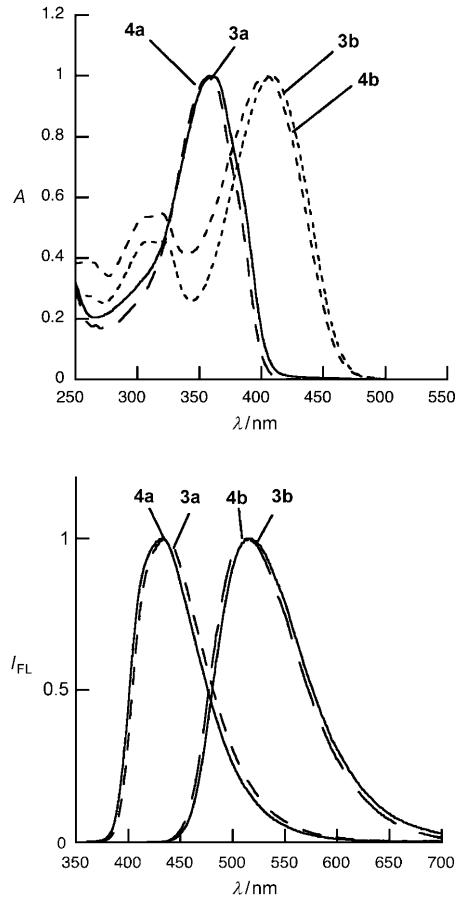


Figure 1. Normalized absorption of phosphane oxide derivatives **3** and **4** chloroform (top) and corrected normalized emission spectra of phosphane oxide derivatives **3** and **4** in chloroform (bottom).

tense band in the near UV/Vis blue region. A noticeable bathochromic shift of both the absorption and the emission spectra was observed by replacing the triple bond by a double bond (Table 1), in agreement with increased electronic conjugation.

As reported earlier for quadripolar fluorophores,[16] a 40 % decrease in the fluorescence quantum yield is observed by replacing the PE_2 bridge with a PE–PV bridge. This is most probably related to the decreased rigidity of the conjugated path in the PE–PV bridge, thereby leading to larger conformational flexibility favoring nonradiative deactivation processes. As expected, a marked bathochromic shift of the absorption and emission spectra is

Table 1. Photophysical properties of compounds **1–6** in chloroform.

Compounds	λ_{max}^{abs} [nm]	$10^{-4}\ \varepsilon_{max}$ [$M^{-1}cm^{-1}$]	λ_{max}^{em} [nm]	Φ[a]	Slope [$10^3\ cm^{-1}$][b]
1a	338	17.7	392	0.77	13.7
2a	335	5.9	388	0.76	13.5
1b	369	12.5	478	0.56	26.0
2b	369	4.1	471	0.66	27.1
3a	361	12.4	435	0.34	13.2
4a	359	5.2	434	0.34	13.3
3b	409	12.2	518	0.43	18.3
4b	404	3.6	516	0.34	18.3
5a	356	11.9	438	0.49	13.2
6a	360	4.18	435	0.45	12.5
5b	408	11.2	523	0.49	21.6
6b	405	3.5	515	0.49	20.1

[a] Fluorescence quantum yield. [b] Slope value derived from the linear variation of the Stokes shifts on the polarity–polarizability function of the solvent (Lippert–Mataga correlation).

observed by increasing the electron-donating strength of the peripheral groups (**1b** (**2b**–**6b**, respectively) versus **1a** (**2a**–**6a**, respectively)). This also leads to a slight decrease in the fluorescence quantum yield in the case of compounds containing the PE_2 bridge, whereas no such effect is observed in the case of compounds for which the PE_2 bridge has been replaced by the PE–PV bridge (**3**–**4**). The replacement of the PO acceptor moiety by the PS core induces only a slight hypochromic shift of the absorption and a slight bathochromic shift of the emission band as well as a definite increase in the fluorescence quantum yield (Table 1).

The effect of coupling several dipolar branches with a common electron-withdrawing PO or PS moiety is already noticeable on the absorption properties. Comparison of the absorption properties of three-branched compound **3b** and its monomeric analogue **4b** shows a redshift and an increase in the maximum molar extinction coefficient per subchromophore in the branched system (Table 1). A slight bathochromic and hyperchromic shift of the absorption band is

also observed in the case of the branched compound **5b** relative to its monomeric analogue **6b**. In the case of the **3a**/**4a** pair, the effect is only a slight redshift for the three-branched system as well as a broadening and consequent decrease in the maximum molar extinction coefficient per subchromophore. In the case of the **5a**/**6a** pair, a slight blueshift and a definite broadening of the low-energy absorption band (showing a clear shoulder at lower wavelengths) and consequent decrease in maximum molar extinction coefficient per subchromophore (Table 1) is observed in the three-branched system. The observed changes of absorption properties when comparing three-branched derivatives with their monomeric analogues demonstrate that interactions take place between branches.

The emission bands of the three-branched phosphane oxide and sulfide compounds are very similar to those of their dipolar counterparts but are slightly redshifted as shown in Figure 1 b. From Table 1, we observe that the redshift depends on the nature of the end groups and connectors. Larger redshifts are observed for more rigid connectors (**1a** vs **2a** and **1b** vs **2b** relative to **3a** vs **4a** and **3b** vs **4b**). In addition, a stronger donor leads to more pronounced redshifts (in particular in the case of **1b** and **5b**). Such a redshift can be related to the proximity of dipolar branches in relation with localization of emission (vide infra). Indeed stronger electron donors lead to larger dipole moments and thus generate larger dipole–dipole interactions between subchromophores in three-branched systems.

Nature of the Emitting Excited State

The solvatochromic behavior of PO and PS was investigated to gain information about the nature of the excited state of the star-shaped (i.e., three-branched) systems. In particular, solvatochromic effects of the new fluorophores (**3**–**4** and **5**–**6**) were studied and compared with the previously observed PO derivatives data. As was reported earlier for derivatives **1**–**2**,[5] increased polarity produces an important bathochromic shift of the emission spectra but only a slight redshift of the absorption spectra (Figure 2). This is a clear signature of an intramolecular charge-transfer transition with a significant increase in dipole moment in the excited state, thereby leading to highly polar excited states.

Interestingly the solvatochromic behavior of the three-branched derivative **3b** is found to be similar to that of its monomeric dipolar analogue **4b**. Hence, the emissive excited state of the three-branched system is also strongly dipolar. Such phenomenon is also observed for compounds **3a** and **4a** (see Figure S2′ in the Supporting Information). Such behavior is similar to that reported for three-branched octupolar systems built from a common triphenylamine donor core[8–10] and points to excitation localization on one of the branches of the branched derivatives occurring after excitation, prior to emission. Further information on the polarity of the excited state of the various phosphane oxide and sulfide derivatives can be gained by examination of the variation in the Stokes shifts function of polarity. This variation

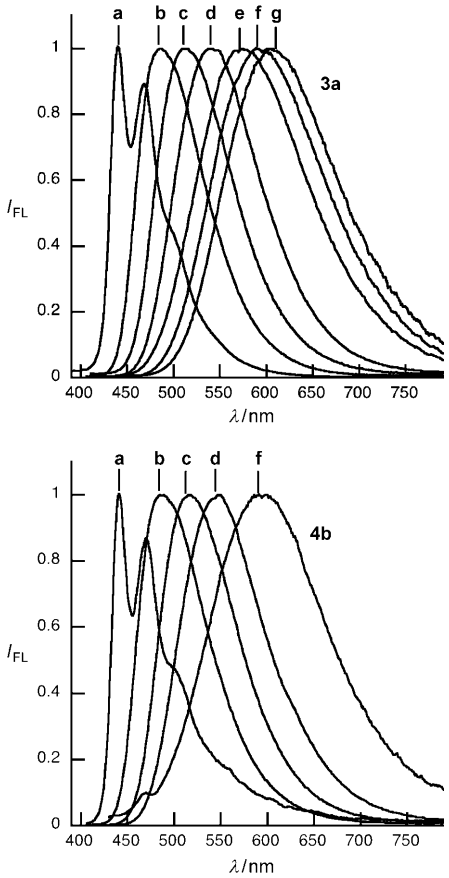


Figure 2. Corrected normalized emission spectra of compounds **3b** (top) and **4b** (bottom) in different solvents: a) Cyclohexane, b) dioxane, c) $CHCl_3$, d) CH_2Cl_2, e) EtOH, f) CH_3CN, g) DMSO. DMSO = dimethyl sulfoxide.

can be fitted by using the well-known Lippert–Mataga equation[21] (Figure 3):

$$\nu_a - \nu_b = \frac{2}{hca^3}(\mu_e - \mu_g)^2 \Delta f + C \quad (1)$$

in which ν_a and ν_f are the maximum absorption and fluorescence wavenumber, respectively, h is Planck's constant, c is the velocity of light, a is the radius of the cavity, μ_e and μ_g are the excited and ground-state dipole moments, and Δf is the orientation polarizability defined as:

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

in which ε is the static dielectric constant and n the optical refractive index of the solvent.

As shown in Figure 3, in which the Stokes shift values in various solvents are plotted against Δf, for several PO derivatives, a linear dependency is obtained, thus allowing the determination of the slope values (Table 1). The slope values are directly related to $\Delta\mu/a^3$ thus giving information on the

CHEMISTRY
AN ASIAN JOURNAL

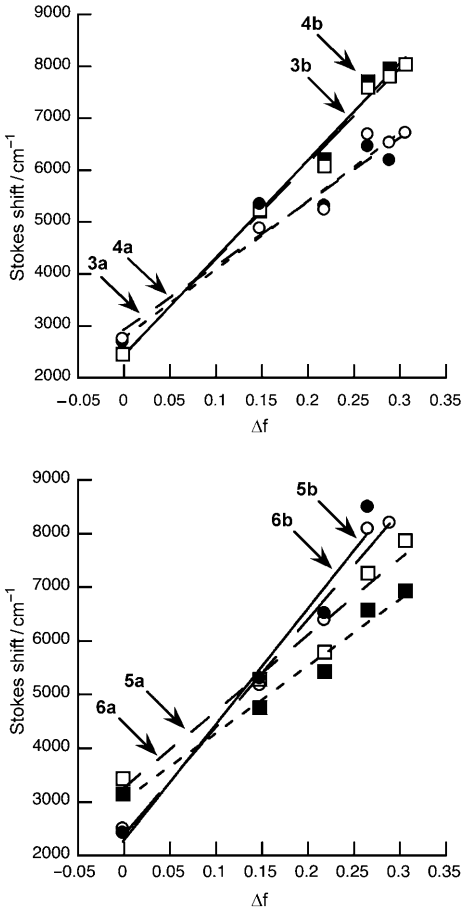


Figure 3. Lippert–Mataga correlations for phosphane oxide fluorophores **3a**, **3b**, **4a**, and **4b** (top) and phosphane sulfide fluorophores **5a**, **5b**, **6a**, and **6b** (bottom).

polarity of the excited states of the different compounds. The change in dipole moment values can then be derived if accurate cavity size can be estimated for such compounds. Alternatively, comparison of the slope values obtained for chromophores of similar shape and size provides valuable information on the polarity of the emitting excited states. As clearly seen in Figure 3 and noted from Table 1, three-branched phosphane oxides show similar solvatochromic amplitude as their one-branch counterpart. This confirms that emission originates from a dipolar branch (acting as a subchromophore) due to excitation localization. We also observe from comparison of phosphane oxide and sulfide derivatives that compounds bearing the stronger dialkylamino donor (derivatives **b**) always show more pronounced solvatochromic behavior (i.e., larger slope values) than their analogues bearing weaker electron-donating alkoxide end groups (Figure 3a). Since the cavity sizes are the same between pairs of **a** and **b** derivatives; this provides evidence that the dialkyamino compounds lead to more polar excited states. Similarly, sulfide derivatives show larger slope values than the corresponding oxide derivatives (Figure 3b), indicative of more polar emitting excited states. In contrast, the slope values are found to be somewhat smaller when comparing related derivatives containing PE–PV bridges and a PE_2 conjugated path (**1a–b** vs **3a–b**, **2a–b**), thereby providing evidence that the triple bond leads to larger dipole moments in the excited state than for analogues with a double bond. Such an effect is most probably related to the rigidity of the linker as was observed earlier for one-dimensional push–pull compounds containing different conjugated paths and acceptor end groups (i.e., push–pull carotenoids and polyenes).[22,23]

To further characterize the photophysical properties of the synthesized compounds, time-resolved fluorescence measurements were performed by using the single-photon-counting method with picosecond laser excitation. The fluorescence decays of phosphane oxide derivatives with PE–PV linkers are displayed in Figure 4. The time constants obtained by decay analysis for the phosphane oxide and sulfide derivatives are gathered in Table 2.

For the compounds containing PE_2 bridges (both mono- and trisubstituted arms), satisfactory fits can be obtained by considering a single exponential ($\chi^2_R < 1.25$). For the compounds containing a PE–PV bridge, monoexponential decays were obtained for the monosubstituted fluorescent arm (compounds **4a** and **4b**). In contrast, satisfactory fits are obtained only by considering two (phosphane sulfide de-

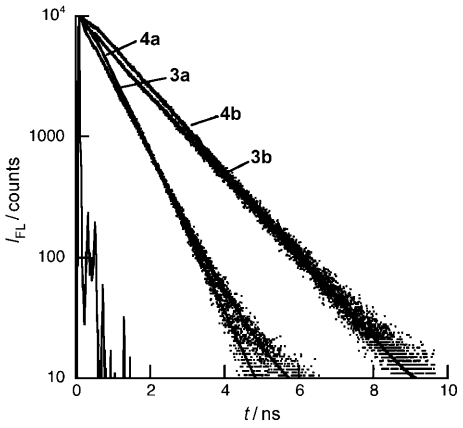


Figure 4. Fluorescence decays of the compounds **3a**, **3b**, **4a**, and **4b** in chloroform.

Table 2. Fluorescence decay components α_i and τ_i of compounds **1–6** in chloroform.

Product	τ_1 [ns] (α_1)	τ_2 [ns] (α_2)	τ_3 [ns] (α_3)	χ^2_R
1a	0.74 (1)			1.05
2a	0.78 (1)			1.02
1b	1.52 (1)			1.07
2b	1.52 (1)			
3a	0.70 (0.72)	0.12 (0.27)	2.17 (0.01)	1.10
4a	0.65 (1)			1.03
3b	1.28 (0.74)	0.18 (0.25)	4.01 (0.01)	1.11
4b	1.24 (1)			1.33
5a	0.72 (0.88)	0.09 (0.12)		1.09
6a	0.69 (1)			1.07
5b	1.36 (0.83)	0.22 (0.17)		1.14
6b	1.24 (1)			1.07

rivatives) or three exponentials (phosphane oxide derivatives) for the three-branched fluorescent compounds (Figure 4). The main lifetime is similar to that of the related rod-shaped derivatives, in agreement with localization of the excitation on one of the subchromophoric branches. Additional lifetimes suggest that interactions occur in the excited state of compounds **3a**–**b** and **5a**–**b** due to the conformationnal flexibility ((*S*)-*cis* to (*S*)-*trans*) they provide. Indeed interactions between the excited subchromophoric branch and other branches can lead to the formation of an "internal" excimer. Such phenomena have been reported earlier in the case of multichromophoric derivatives for which push–pull compounds are grafted in close proximity on a common platform by a short flexible linker[24] and in the case of bidentate PO derivatives.[7]

Two-Photon Properties

The TPA characteristics of compounds **1**–**6** were determined in the 700–1000 nm spectral region by studying their two-photon excited fluorescence, following the methodology described by Webb and collaborators, and by using fs pulse excitation and fluorescein as a reference compound. The TPA data measured in chloroform are collected in Table 3. In all cases we observe that the lowest energy band peaks at about half the energy (i.e., twice the wavelength) of the lowest energy one-photon absorption band, which indicates that the lowest excited state is both one and two-photon allowed.

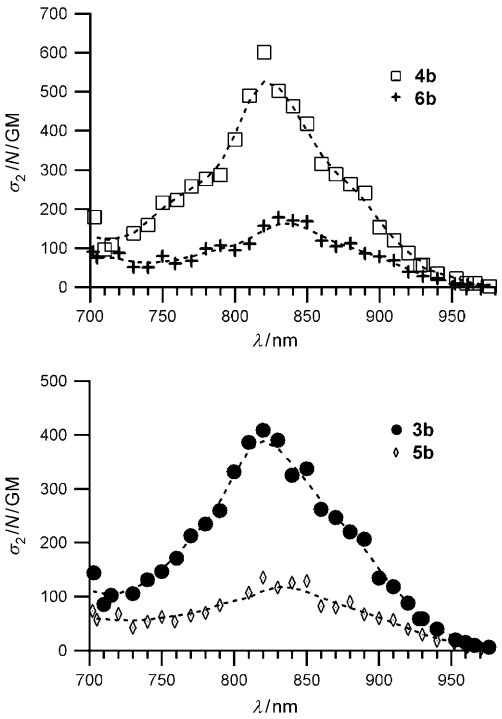


Figure 5. TPA spectra of **4b**/**6b** (top; □ = **4b**, + = **6b**) and **3b**/**5b** (bottom; ● = **3b**, ◇ = **5b**) in chloroform.

Core Effect: TPPO Versus TTPS

As clearly evidenced from Table 3 and illustrated in Figure 5, the phosphane sulfides show much lower TPA responses than the corresponding phosphane oxides. The slight redshift of the TPA peaks parallels the effect observed for OPA peaks. However, the reduction in TPA cross-sections is much more pronounced than the hypochromic shift of the OPA band. The TPA peak cross-sections in the NIR region are typically reduced by a factor of three to four, whereas extinction coefficients are reduced by only 10 to 20% (Table 1).

End-Group Effect: Donor Strength

For all phosphane oxide and sulfide derivatives, increasing the strength of electron-donating end groups results in a significant bathochromic shift and pronounced enhancement of the TPA band (Figure 6). Here again, the redshift of the TPA band parallels the redshift of the OPA band. However, whereas stronger electron-donating terminal groups generate a slight decrease in OPA, a major increase in the TPA cross-sections in the NIR region is obtained, typically by a factor of three to five for the peak TPA cross-sections (Table 3).

Table 3. Two-photon absorption properties of compounds **1**–**6** in chloroform.

Product	N_{eff}[a]	λ_{TPA}^{max} [nm]	σ_2^{max}[b] [GM]	σ_2^{max}/N[c] [GM]	σ_2^{max}/M_W [GM g^{-1} mol]	σ_2^{max}/N_{eff} [GM]
1a	38.2	<700	>135	>45	>0.139	>3.5
2a	23.7	<700	>150	>50	>0.295	>6.3
1b	38.2	760	600	200	0.595	15.7
2b	23.7	760	180	180	0.435	7.6
3a	38.2	750	360	120	0.284	9.4
4a	23.7	750	145	145	0.238	6.1
3b	38.2	820	1300	420	0.811	34.1
4b	23.7	820	650	650	0.903	27.5
5a	38.2	740	120	40	0.093	3.1
6a	23.7	750	85	85	0.136	3.6
5b	38.2	820	420	140	0.259	11.0
6b	23.7	830	170	170	0.231	7.2

[a] Effective number of π electrons in the conjugated systems.[25] [b] TPA cross-section at maximum, 1 GM = 10^{-50} cm^4 s.photon^{-1}. [c] Maximum TPA cross-section normalized with respect to the number of branches (*N*), the number of π electrons (N_{eff}), or the molecular weight (M_W).

Connector Effect: Phenylene–Vinylene (PV) Versus Phenylene–Ethynylene (PE) Moieties

Replacing a phenylene–vinylene unit by a phenylene–ethynylene unit in the conjugated linker between the PO core and the donating end groups also induces a significant bathochromic shift of the TPA spectra, and leads to a major increase in

CHEMISTRY
AN ASIAN JOURNAL

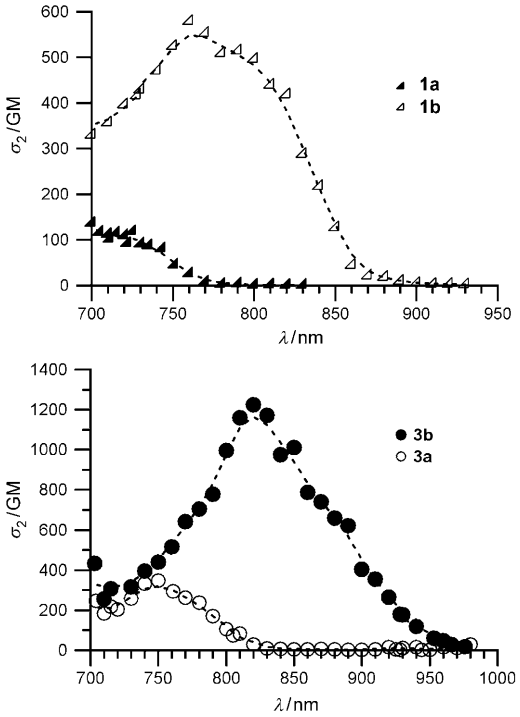


Figure 6. TPA spectra of **1a/1b** (top; ▲=**1a**, △=**1b**) and **3a/3b** (bottom; ○=**3a**, ●=**3b**) in chloroform.

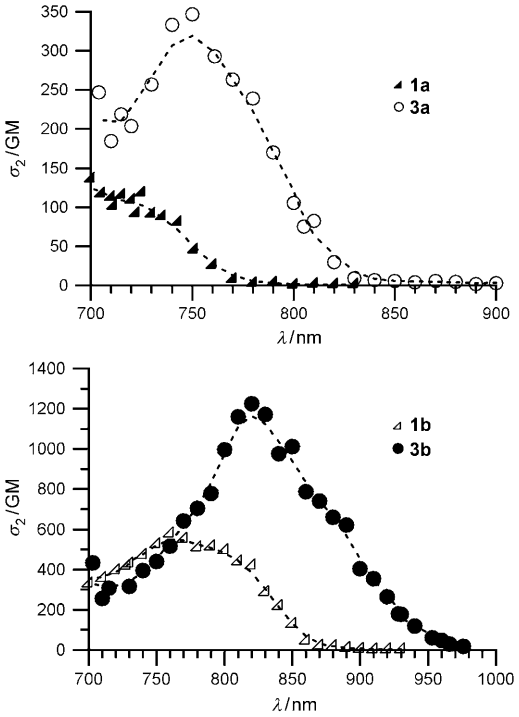


Figure 7. TPA spectra of **1a/3a** (top; ▲=**1a**, ○=**3a**) and **1b/3b** (bottom; △=**1b**, ●=**3b**) in chloroform.

the TPA cross-sections in the NIR region (Figure 7). The peak TPA cross-sections are enhanced by a factor of two to three (the stronger enhancement being obtained for a stronger terminal donor), whereas the maximum extinction coefficients are found to decrease (the stronger donors also giving rise to the larger effect). Hence, in that case, opposite effects are obtained for OPA and TPA. Replacement of the PE2 linker by the PE–PV linker is thus a successful strategy, as was already observed in the case of symmetrical quadrupolar derivatives.[16]

Branching Effect

To examine the effect of coupling between branches on TPA responses, we have compared the response per subchromophore (Figure 8) for all pairs of derivatives (three-branched vs monomeric compound). In the case of phosphane oxides containing a PE_2 connector, we observe that the coupling with a common PO electron-withdrawing moiety leads to a very slight enhancement of TPA response following the trend observed for OPA. Hence, in the case of such rigid compounds, the slight electronic coupling between branches results in weak enhancement of both OPA and TPA. In the case of phosphane oxide and sulfide derivatives containing a PE–PV connector coupling leads instead to a marked broadening of the TPA band and a consequent small decrease in the peak TPA responses. This effect can be related to the conformational flexibility of the PE–PV linker.

To further examine the effect of coupling between branches on the TPA in phosphine oxide and sulfide derivatives, we have compared the normalized TPA response by using two different normalization procedures. The first one, which is relevant for applications, such as optical limitation,[10] is based on the molecular weight (M_W). The different σ_2^{max}/M_W values determined for the various derivatives are gathered in Table 3. In the case of the PE_2 derivatives, we observe a major enhancement of the σ_2^{max}/M_W value for the three-branched derivatives, whereas the PE–PV derivatives show different trends depending on the nature of the donor end groups or the core (PS versus PO). A slight enhancement is obtained only for PO derivatives containing the alkoxy donor end groups or the PS derivatives containing the dialkyamino donor end groups. The second normalization procedure based on the number of conjugated π-electrons (N_{eff})[25] gives more precise information on the intrinsic effect of coupling between branches in phosphane oxide and sulphide derivatives. As clearly shown in Table 3, the σ_2^{max}/N_{eff} values are larger for the three-branched derivatives except in the case of the sulfide derivative **5a**, which is the only derivative for which branching leads to a blueshift of the low-energy absorption band. As was the case with other normalization criteria, the PE_2 linker leads to the steepest effect, which confirms that the rigidity of the branches plays an important role in promoting enhancement of the TPA response in TPPO and TPPS three-branched derivatives.

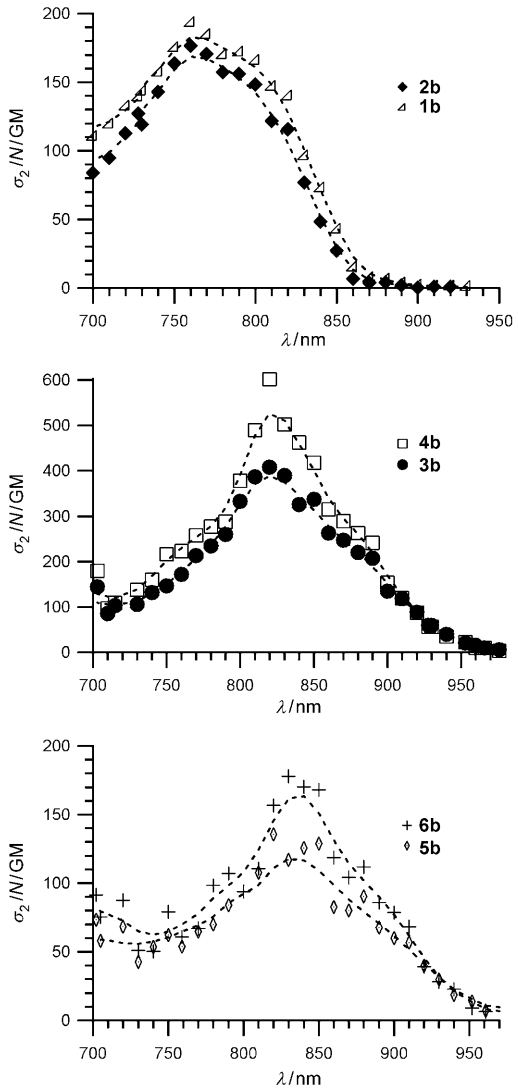


Figure 8. TPA spectra of **1b/2b** (top; ◆ = **2b**, △ = **1b**), **3b/4b** (middle; □ = **4b**, ● = **3b**), and **5b/6b** (bottom; + = **6b**, ◇ = **5b**) in chloroform.

Conclusions

New rod-shaped and three-branched derivatives formed by the coupling of dipolar branches based on PE–PV conjugated linkers with a common PO or PS core have been prepared and investigated. Photophysical studies show that all compounds combine significant fluorescence and TPA response in the NIR region. Time-resolved fluorescence decay and solvatochromic studies indicate that excitation is localized on one of the branches, leading to highly dipolar excited states. As a result, the chromophores behave as fluorescence polarity probes for polarity sensing. In addition, the excited state polarity can be significantly enhanced by selecting appropriate conjugated linkers and terminal moieties: stronger donating end groups, TTPS core, and more rigid linkers lead to a greater sensitivity to polarity. In addition, OPA intensities are only weakly affected by the nature of donating end groups or the conjugated linkers, whereas stronger donor groups and PE–PV linkers allow the enhancement of TPA responses in a significant way. This study thus opens a promising route towards new biphotonic environment sensitive probes by the suitable combination of donor end groups (powerful donor groups), acceptor TPPO moieties, and conjugated linkers (elongated systems based on PE–PV linkers) to ensure both highly environment-dependent fluorescence and very large TPA responses. This is of high interest for sensing in media for which endogenous fluorophores or fluorescent contaminants are present. It should be stressed that the modularity of synthesis allows variation of the structure to modify the affinity/solubility of such compounds.

Finally, coupling between branches leads to either a very slight enhancement of TPA response per subchromophoric unit (branch) or to broadening of the TPA band in the NIR region and subsequent decrease in the peak TPA cross-sections. This study thus shows that TPPO and TPPS cores do not promote major cooperative enhancement of the TPA responses, as was the case for branched octupolar derivatives built from a common electron-donating triphenylamine core (leading to the rise of an intense TPA band at higher energy)[10–14,26–27] or from a common connecting benzene moiety (leading to enhancement of the low-energy TPA band),[28] but rather lead to TPA broadening. Such behavior is closer to that reported for octupolar derivatives built from a triphenylbenzene core,[15] which suggests that TPPO and TPPS cores do not promote coherent coupling between branches but instead through-space electrostatic interactions between dipolar subchromophores are responsible for modifications of the TPA responses of the branched phosphane oxide and sulfide compounds.[29]

Experimental Section

Synthesis of Phosphane Derivatives

Reagents were commercially available from Acros and Aldrich and used without further purification unless otherwise stated. Column chromatography was performed with E. Merck 0.040–0.063 mm Art. 11567 silica gel. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AV 400 instrument. Chemical shifts were reported downfield from Me_4Si (δ = 0 ppm) for ^{1}H and ^{13}C spectroscopy, and H_3PO_4 was used as an internal standard for ^{31}P NMR spectroscopy. Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. MS analyses were performed at IMAGIF/ICSN and at the University P. et M. Curie. Compounds **1**–**2**, **8**–**9**, and **8′** were prepared according to previously published procedures.[3,5,6] Compounds **11** and **12** were also prepared according to published procedures.[16,19]

*Phosphane Oxide **3a***

CuI (4 mg, 0.021 mmol) and $[PdCl_2(PPh_3)_2]$ (5 mg, 0.007 mmol) were added to a solution of [(*E*)-1-iodo-4-(4-octyloxy)styryl]benzene (236 mg, 0.54 mmol), tris(4-ethynylphenyl)phosphane oxide (48 mg, 0.136 mmol) in a mixture of toluene (5 mL), and diisopropylamine (3 mL). The resulting mixture was stirred for 15 h at 50 °C, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (dichloromethane/methanol 98:2) to give the product (147 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.70 (m, 12H; ArH), 7.44–7.54 (m, 18H; ArH), 7.11 (d, 3H, J = 16.0 Hz; HC=C), 6.96

(d, 3H, J=16.0 Hz; Hvin), 6.90 (d, 6H, J=8.7 Hz; ArH), 3.98 (t, 6H, J=6.6 Hz), 1.79 (m, 6H), 1.40–1.50 (m, 6H), 1.25–1.40 (m, 24H), 0.89 ppm (t, 9H, J=6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.4 (3C), 138.5 (3C), 132.2 (6C), 132.1 (d, J=10.5 Hz, 6C), 131.7 (d, J=12.4 Hz, 6C), 131.7 (d, 3C), 129.8 (3C), 129.7 (3C), 128.0 (6C), 127.7 (3C), 126.3 (6C), 125.7 (3C), 121.1 (3C), 114.9 (6C), 92.9 (3C), 89.2 (3C), 68.3 (3C), 32.0 (3C), 29.5 (3C), 29.4 (6C), 26.2 (3C), 22.8 (3C), 14.3 ppm (3C); ^{31}P NMR (162 MHz, $CDCl_3$): δ=28.9 ppm; HRMS (ESI+): m/z: calcd for $C_{90}H_{94}O_4P$: 1269.6884; found: 1269.6937 $[M+H]^+$.

Phosphane Oxide ***4a***

CuI (9 mg, 0.047 mmol) and $[PdCl_2(PPh_3)_2]$ (11 mg, 0.015 mmol) were added to a solution of [(*E*)-1-iodo-4-(4-octyloxy)styryl]benzene (273 mg, 0.628 mmol), diphenyl(4-ethynylphenyl)phosphane oxide (95 mg, 0.314 mmol) in a mixture of toluene (10 mL), and diisopropylamine (5 mL). The resulting mixture was stirred for 15 h at 50 °C, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (dichloromethane/methanol 98:2) to give the product (151 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54–7.72 (m, 10H; ArH), 7.44–7.54 (m, 10H; ArH), 7.10 (d, 1H, J=16.0 Hz; HC=C), 6.95 (d, 1H, J=16.0 Hz; HC=C), 6.89 (d, 2H, J=8.7 Hz; ArH), 3.98 (t, 2H, J=6.7 Hz), 1.79 (m, 2H), 1.45 (m, 2H), 1.20–1.40 (m, 8H), 0.89 ppm (t, 3H, J=6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.4 (C), 138.4 (C), 132.4 (d, J=103.9 Hz, 2C), 132.3 (d, J=103.9 Hz, C), 132.2 (d, 2C), 132.2 (2C), 132.1 (d, 4C), 132.1 (d, 2C), 131.5 (d, 2C), 129.7 (C), 129.7 (C), 128.7 (d, J=11.5 Hz, 4C), 128.0 (2C), 127.4 (C), 126.3 (2C), 125.7 (C), 121.1 (C), 114.9 (2C), 92.6 (C), 89.3 (C), 68.3 (C), 32.0 (C), 29.5 (C), 29.4 (2C), 26.2 (C), 22.8 (C), 14.3 ppm (C); ^{31}P NMR (162 MHz, $CDCl_3$): δ=29.6 ppm; HRMS (ESI+): m/z: calcd for $C_{42}H_{42}O_2P$: 609.2917; found: 609.2891 $[M+H]^+$.

Phosphane Oxide ***3b***

CuI (4 mg, 0.021 mmol) and $[PdCl_2(PPh_3)_2]$ (5 mg, 0.007 mmol) were added to a solution of (*E*)-4-(4-iodostyryl)-*N*,*N*-dioctylaniline (297 mg, 0.54 mmol), tris(4-ethynylphenyl)phosphane oxide (48 mg, 0.136 mmol) in a mixture of toluene (5 mL), and diisopropylamine (3 mL). The resulting mixture was stirred for 15 h at 50 °C, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (dichloromethane/methanol 98:2) to give the product (192 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.61–7.78 (m, 12H; ArH), 7.42–7.52 (m, 12H; ArH), 7.38 (d, 6H, J=8.7 Hz; ArH), 7.06 (d, 3H, J=16.0 Hz; HC=C), 6.85 (d, 3H, J=16.5 Hz; HC=C), 6.61 (d, 6H, J=8.7 Hz; ArH), 3.28 (t, 12H, J=7.6 Hz), 1.59 (m, 12H), 1.20–1.35 (m, 60H), 0.89 ppm (t, 18H, J=6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=148.1 (3C), 139.1 (3C), 132.2 (d, J=10.5 Hz; 6C), 132.1 (6C), 131.6 (d, J=12.4 Hz; 6C), 131.4 (d, 3C), 130.4 (3C), 128.1 (6C), 127.8 (3C), 125.9 (6C), 124.0 (3C), 122.6 (3C), 120.1 (3C), 111.6 (6C), 93.1 (3C), 88.9 (3C), 51.1 (6C), 31.9 (6C), 29.6 (6C), 29.4 (6C), 27.4 (6C), 27.3 (6C), 22.8 (6C), 14.3 ppm (6C); ^{31}P NMR (162 MHz, $CDCl_3$): δ=29.1 ppm; HRMS (ESI+): m/z: calcd for $C_{114}H_{145}N_3OP$: 1603.1119; found: 1603.1192 $[M+H]^+$.

Phosphane Oxide ***4b***

CuI (9 mg, 0.047 mmol) and $[PdCl_2(PPh_3)_2]$ (11 mg, 0.015 mmol) were added to a solution of (*E*)-4-(4-iodostyryl)-*N*,*N*-dioctylaniline (343 mg, 0.628 mmol), diphenyl(4-ethynylphenyl)phosphane oxide (95 mg, 0.314 mmol) in a mixture of toluene (10 mL), and diisopropylamine (5 mL). The resulting mixture was stirred for 15 h at 50 °C, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (dichloromethane/methanol 99:1) to give the product (188 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53–7.72 (m, 10H; ArH), 7.42–7.53 (m, 8H; ArH), 7.38 (d, 2H, J=9.2 Hz; ArH), 7.07 (d, 1H, J=16.5 Hz; HC=C), 6.85 (d, 1H, J=16.5 Hz; HC=C), 6.61 (d, 2H, J=9.2 Hz; ArH), 3.28 (t, 4H, J=7.6 Hz), 1.59 (m, 4H), 1.20–1.40 (m, 20H), 0.89 ppm (t, 6H, J=6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ=148.2 (C), 139.2 (C), 132.4 (d, J=103.9 Hz, 2C), 132.2 (d, 4C), 132.2 (d, 2C), 132.1 (2C), 132.1 (d, 2C), 132.0 (d, J=103.9 Hz, C), 131.5 (d, J=12.4 Hz, 2C), 130.4 (C), 128.7 (d, J=12.4 Hz, 4C), 128.2 (2C), 127.5 (C), 126.0 (2C), 124.1 (C), 122.7 (C), 120.2 (C), 111.7 (2C), 92.9 (C), 89.0 (C), 51.2 (2C), 32.0 (2C), 29.6 (2C), 29.5 (2C), 27.5 (2C), 22.8 (2C), 14.3 ppm (2C); ^{31}P NMR (162 MHz, $CDCl_3$): δ=29.6 ppm; HRMS (ESI+): m/z: calcd for $C_{50}H_{39}NOP$: 720.4328; found: 720.4347 $[M+H]^+$.

Phosphane Sulfide ***9′***

Magnesium turnings (100 mg, 4.17 mmol) were placed in a 25 mL Schlenk tube under argon. Distilled tetrahydrofuran (THF; 6 mL) and 4-(bromophenylethynyl)trimethylsilane **5** (992 mg, 4 mmol) were added and the reaction was stirred overnight at room temperature. Chlorodiphenylphosphine (882 mg, 4 mmol) and distilled THF (2 mL) were placed in a 50 mL Schlenk tube under argon at 0 °C. The solution of the Grignard reagent was added dropwise over 15 min. The reaction mixture was allowed to warm up to room temperature and stirred for 1 h. The solution was then filtrated through a pad of silica with diisopropyl ether (20 mL). The solvents are removed in vacuo, the oily residue is redissolved in distilled toluene (30 mL), and sulfur (172 mg, 6 mmol) is added. The reaction mixture was heated to 100 °C for 2 h. The solvents were removed under vacuum and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 90:10) to give [4-(diphenylphosphinothioyl)phenylethynyl]trimethylsilane (450 mg, 1.15 mmol). The oily product is placed in a 100 mL flask and redissolved in a mixture of dichloromethane (20 mL) and methanol (40 mL). Potassium carbonate (159 mg, 1.15 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. The solvents were evaporated under vacuum and the residue redissolved in diisopropyl ether (30 mL). Filtration through a pad of silica and evaporation of the solvents gave the phosphane sulfide **7** (340 mg, 27 %) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.65–7.75 (m, 6H; ArH), 7.40–7.55 (m, 9H; ArH), 3.20 ppm (s, 1H; HC≡C); ^{13}C NMR (75 MHz, $CDCl_3$): δ=133.6 (d, J=85.2 Hz; C), 132.5 (d, J=85.7 Hz; 2C), 132.2 (d, J=10.5 Hz; 4C), 132.1 (d, J=7.2 Hz; C), 132.0 (d, J=8.8 Hz; 2C), 131.7 (d, J=2.8 Hz; C), 128.6 (d, J=12.2 Hz; 4C), 125.5 (d, J=3.3 Hz; 2C), 81.9 (C), 79.3 ppm (C); ^{31}P NMR (121 MHz, $CDCl_3$): δ=43.2 ppm; HRMS (ESI+): m/z: calcd for $C_{20}H_{15}NaPS$: 340.0524; found: 340.0525.

Phosphane Sulfide ***5a***

CuI (4 mg, 0.021 mmol) and $[PdCl_2(PPh_3)_2]$ (5 mg, 0.007 mmol) were added to a solution of [(*E*)-1-iodo-4-(4-octyloxy)styryl]benzene (236 mg, 0.54 mmol), tris(4-ethynylphenyl)phosphane sulfide (50 mg, 0.136 mmol) in a mixture of toluene (3 mL), and diisopropylamine (3 mL). The resulting mixture was stirred for 15 h at 50 °C, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (cyclohexane/dichloromethane 6:5) to give the product (125 mg, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, 9H, J=7 Hz), 1.25–1.55 (m, 30H), 1.74–1.81 (m, 6H), 3.97 (t, 6H, J=7 Hz), 6.89 (d, 12H, J=8.6 Hz), 6.95 (d, 3H, J=16 Hz), 7.10 (d, 3H, J=16 Hz), 7.41–7.53 (m, 16H), 7.59–7.79 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.4 (3C), 138.4 (3C), 137.8 (3C), 132.5 (6C), 132.4 (d, J=10.4 Hz, 6C), 132.2 (6C) , 131.7 (6C), 129;7 (3C), 128.6 (d, J=12.6 Hz, 6C), 128.0 (3C), 126.3 (3C), 125.6 (3C), 121.0 (3C), 114.9 (6C), 92.9 (3C), 89.2 (3C), 68.2 (6C), 31.9 (6C), 29.8 (6C), 29.5 (6C), 29.4 (6C), 26.2 (6C), 22.8 (6C), 14.3 ppm (6C); ^{31}P NMR (121 MHz, $CDCl_3$): δ=42.75 ppm; HRMS (MALDI-TOF): m/z: calcd for $C_{90}H_{94}O_3PS$: 1285.65; found: 1285.65 $[M+H]^+$.

Phosphane Sulfide ***5b***

CuI (4 mg, 0.021 mmol) and $[PdCl_2(PPh_3)_2]$ (5 mg, 0.007 mmol) were added to a solution of (*E*)-4-(4-iodostyryl)-*N*,*N*-dioctylaniline (297 mg, 0.544 mmol), tris(4-ethynylphenyl)phosphane sulfide (50 mg, 0.136 mmol) in a mixture of toluene (3 mL), and diisopropylamine (3 mL). The resulting mixture was stirred at 50 °C for 15 h, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (cyclohexane/dichloromethane 6:4) to give the product (121 mg, 63 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, 18H, J=7 Hz), 1.28–1.31 (m, 48H), 1.55–1.58 (m, 24H), 3.27 (t, 12H, J=7 Hz), 6.61 (d, 12H, J=9 Hz), 6.85 (d, 3H, J=16 Hz), 7.08 (d, 3H, J=16 Hz),

7.36–7.46 (m, 16H), 7.48–7.73 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.2 (3C), 139.1 (3C), 133.3 (6C), 132.9 (3C), 132.4 (d, J=10.5 Hz, 6C), 132.3 (6C), 132.2 (6C), 132.1 (6C),131.4 (d, J=12.3 Hz, 6C) 131.2 (3C), 130.3 (3C), 128.2 (6C), 127.7 (3C), 125.8 (6C), 124.3 (3C), 122.5 (3C), 120.3 (3C), 111.5 (6C), 92.9 (6C),51.2 (6C), 31.9 (6C), 29.9 (6C), 29.4 (6C), 27.4 (6C), 27.3 (6C), 22.8 (6C), 14.2 ppm (6C);^{31}P NMR (121 MHz, $CDCl_3$): δ=42.7 ppm; HRMS (MALDI-TOF): m/z: calcd for $C_{114}H_{145}N_3PS$: 1619.97; found 1619.97 $[M+H]^+$

Phosphane Sulfide ***6a***

CuI (9 mg, 0.047 mmol) and $[PdCl_2(PPh_3)_2]$ (11 mg, 0.015 mmol) were added to a solution of [(*E*)-1-iodo-4-(4-octyloxy)styryl]benzene (273 mg, 0.629 mmol), diphenyl(4-ethynylphenyl)phosphane sulfide (100 mg, 0.314 mmol) in a mixture of toluene (5 mL), and diisopropylamine (3 mL). The resulting mixture was stirred for 15 h at 50 °C, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (cyclohexane/dichloromethane 6:5) to give the product (135 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, 3H, J=7 Hz), 1.29–1.32 (m, 10H), 1.55–1.58 (m, 2H), 3.97 (t, 2H, J=7 Hz), 6.89 (d, 4H, J=8.8 Hz), 6.95 (d, 1H, J=16 Hz), 7.10 (d, 1H, J=16 Hz), 7.43–7.60 (m, 10H), 7.66–7.74 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.3 (C), 138.4 (C), 132.4 (d, J=10.5 Hz, 2C) 132.3 (2C), 132.2 (2C), 131.9 (2C), 131.6 (2C), 131.4 (2C), 129.7 (C), 128.8 (d, J=12 Hz, 2C), 128.0 (2C), 126.9 (2C), 125.6 (C), 121.1 (C), 114.8 (2C), 92.6 (C), 89.2 (C), 51.2 (C), 31.9 (C), 29.6 (C), 29.4 (C), 27.4 (C), 27.3 (C), 22.8 (C), 14.2 ppm (C); ^{31}P NMR (121 MHz, $CDCl_3$): δ=43.22 ppm; HRMS (ESI+): m/z: calcd for $C_{42}H_{42}OPS$: 625.2616; found: 625.2603 $[M+H]^+$.

Phosphane Sulfide ***6b***

CuI (9 mg, 0.047 mmol) and $[PdCl_2(PPh_3)_2]$ (11 mg, 0.015 mmol) were added to a solution of (*E*)-4-(4-iodostyryl)-*N*,*N*-dioctylaniline (342 mg, 0.628 mmol), diphenyl(4-ethynylphenyl)phosphane sulfide (100 mg, 0.314 mmol) in a mixture of toluene (5 mL), and diisopropylamine (3 mL). The resulting mixture was stirred at 50 °C for 15 h, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (cyclohexane/dichloromethane 7:3) to give the product (150 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (t, 6H, J=7 Hz), 1.29–1.32 (m, 20H), 1.55–1.58 (m, 4H), 3.28 (t, 4H, J=7 Hz), 6.62 (d, 4H, J=9 Hz), 6.85 (d, 1H, J=16 Hz), 7.08 (d, 1H, J=16 Hz), 7.37–7.67 (m, 10H), 7.70–7.77 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.2 (C), 139.1 (C), 133.4 (C), 132.4 (d, J=10.4 Hz, 3C), 132.3 (6C), 132.2 (2C), 132.1 (2C), 131.8 (2C), 131.6 (2C), 131.4 (2C), 130.4 (3C), 128.9 (C), 128.7 (d, J=12 Hz, 2C), 128.1 (2C), 125.5 (2C), 124.1 (C), 122.7 (2C), 120.2 (C), 111.6 (2C), 92.9 (C), 88.9 (C), 51.2 (2C), 31.9 (2C), 29.6 (2C), 29.4 (2C), 27.4 (2C), 27.3 (2C), 22.8 (2C), 14.2 ppm (2C); ^{31}P NMR (121 MHz, $CDCl_3$): δ=43.22 ppm; HRMS (ESI+): m/z: calcd for $C_{50}H_{59}NPS$: 736.4028; found: 736.4008 $[M+H]^+$.

Spectroscopic Measurements

UV/Vis absorption spectra were recorded on a Varian Cary5E spectrophotometer. Corrected emission spectra were obtained on a Jobin–Yvon Spex FluoroMax spectrofluorometer. Cyclohexane, dioxane, chloroform, dichloromethane, dimethylsulfoxide, acetonitrile, and ethanol (Aldrich, spectrometric grade or SDS, spectrometric grade) were employed as solvents for absorption and fluorescence measurements. The fluorescence quantum yields were determined by using quinine sulfate dihydrate in sulfuric acid (0.5 N) as a standard (Φ=0.546).[30] The estimated experimental error is less than 10%. For the emission measurements, the absorbance at the excitation wavelength are kept below 0.1 and the concentration are then below 10^{-5} for the dipolar compounds and 10^{-6} mol L^{-1} for the three-branched compounds. Fluorescence intensity decays were obtained by the single-photon timing method with picosecond laser excitation by using a Spectra-Physics set-up composed of a Titanium Sapphire Tsunami laser pumped by an argon ion laser, a pulse detector, and doubling (LBO) and tripling (BBO) crystals. Light pulses were selected by optoacoustic crystals at a repetition rate of 4 MHz. Fluorescence photons were detected through a long-pass filter (375 nm) by means of a Hamamatsu MCP R3809U photomultiplier, connected to a constant fraction discriminator. The time-to-amplitude converter was purchased from Tennelec. Data were analyzed by a nonlinear least-squares method by using Globals software (Globals Unlimited, University of Illinois at Urbana-Champaign, Laboratory of Fluorescence Dynamics).

Two-Photon Absorption Experiments

TPA spectra were obtained by measuring the TPEF (two-photon excited fluorescence) according to the well-established method described by Xu and Webb[31] and the appropriate solvent-related refractive index corrections.[32] TPEF cross-sections were measured relative to fluorescein in 0.01 M aqueous NaOH for 715–980 nm.[31,33] Data points between 700 and 715 nm were corrected according to reference.[34] A mode-locked Ti:sapphire laser generating 150 fs wide pulses at a rate of 76 MHz, with a time-averaged power of several hundreds of mW (Coherent Mira 900 pumped by a 5 W Verdi) was used as the excitation source. The excitation was focused into the cuvette through a microscope objective (10×, NA 0.25). The fluorescence was detected in epifluorescence mode by a dichroic mirror (Chroma 675dcxru) and a barrier filter (Chroma e650sp-2p) by a compact CCD spectrometer module BWTek BTC112E. Total fluorescence intensities were obtained by integrating the corrected emission spectra measured by this spectrometer.TPA cross-sections (σ_2) were determined from the two-photon excited fluorescence (TPEF) cross-sections ($\sigma_2\Phi$) and the fluorescence emission quantum yield (Φ).

Acknowledgements

We are grateful to A. Brosseau for his assistance in tuning the single-photon timing instruments. We thank Dr. O. Mongin for helpful discussions. This work was supported by the French Agence Nationale pour la Recherche (grant no. ANR-08-CP2D-11). Région Bretagne is gratefully acknowledged for a fellowship to C.R.

[1] M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu, *Science* **1998**, *281*, 1653–1657.
[2] B. Valeur, *Molecular Fluorescence. Principles and Applications*, Wiley-VCH, Weinheim, **2002**.
[3] M. H. Ha-Thi, V. Souchon, M. Penhoat, F. Miomandre, J. P. Genet, I. Leray, V. Michelet, *Lett. Org. Chem.* **2007**, *4*, 185–188.
[4] M. H. Ha-Thi, M. Penhoat, V. Michelet, I. Leray, *Org. Lett.* **2007**, *9*, 1133–1136.
[5] M. H. Ha-Thi, V. Souchon, A. Hamdi, R. Metivier, V. Alain, K. Nakatani, P. G. Lacroix, J. P. Genet, V. Michelet, I. Leray, *Chem. Eur. J.* **2006**, *12*, 9056–9065.
[6] R. Métivier, R. Amengual, I. Leray, V. Michelet, J. P. Genêt, *Org. Lett.* **2004**, *6*, 739–742.
[7] M.-H. Ha-Thi, M. Penhoat, D. Drouin, M. Blanchard-Desce, V. Michelet, I. Leray, *Chem. Eur. J.* **2008**, *14*, 5941–5950.
[8] L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2004**, *6*, 47–50.
[9] C. Le Droumaguet, O. Mongin, M. H. V. Werts, M. Blanchard-Desce, *Chem. Commun.* **2005**, 2802–2804.
[10] C. Katan, F. Terenziani, O. Mongin, M. H. V. Werts, L. Porrès, T. Pons, J. Mertz, S. Tretiak, M. Blanchard-Desce, *J. Phys. Chem. A* **2005**, *109*, 3024–3037.
[11] A. Bhaskar, G. Ramakrishna, Z. Lu, R.; Twieg, J. M. Hales, D. J. Hagan, E. Van Stryland, T. Goodson, III, *J. Am. Chem. Soc.* **2006**, *128*, 11840–11849; Twieg, J. M. Hales, D. J. Hagan, E. Van Stryland, T. Goodson, III, *J. Am. Chem. Soc.* **2006**, *128*, 11840–11849.
[12] T. G. Goodson, III, *Acc. Chem. Res.* **2005**, *38*, 99–107.
[13] C. Katan, F. Terenziani, C. Le Droumaguet, O. Mongin, M. H. V. Werts, S. Tretiak, M. Blanchard-Desce, *Proc. SPIE-Int. Soc. Opt. Eng.* **2005**, *5935*, 13–27.

[14] F Terenziani, C Katan, E Badaeva, S. Tretiak, M. Blanchard-Desce, *Adv. Mater.* **2008**, *20*, 4641 – 4678.
[15] F. Terenziani, C. Le Droumaguet, C. Katan, O. Mongin, M. Blanchard-Desce, *ChemPhysChem* **2007**, *8*, 723 – 734.
[16] O. Mongin, L. Porrès, M. Charlot, C. Katan, M. Blanchard-Desce, *Chem. Eur. J.* **2007**, *13*, 1481 – 1498.
[17] a) O. Mongin, L. Porrès, L. Moreaux, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2002**, *4*, 719 – 722; b) L. Porrès, B. K. G. Bhatthula, M. Blanchard-Desce, *Synthesis* **2003**, 1541 – 1544.
[18] V. Alain, S. Rédoglia, M. Blanchard-Desce, S. Lebus, K. Lukaszuk, R. Wortmann, U. Gubler, C. Bosshard, P. Günter, *Chem. Phys.* **1999**, *245*, 51 – 71.
[19] H. Ndayikengurukiye, S. Jacobs, W. Tachelet, J. Van Der Looy, A. Pollaris, H. J. Geise, M. Claeys, J. M. Kauffmann, S. Janietz, *Tetrahedron* **1997**, *53*, 13811 – 13828.
[20] a) R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874 – 922; b) H. Doucet, J.-C. Hierso, *Angew. Chem.* **2007**, *119*, 850 – 888; *Angew. Chem. Int. Ed.* **2007**, *46*, 834 – 871.
[21] a) N. Mataga, Y. Kaifu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690 – 691; b) E. Z. Lippert, *Z. Naturforsch. A* **1955**, *10*, 541 – 545.
[22] M. Blanchard-Desce, R. Wortmann, S. Lebus, J.-M. Lehn, P. Krämer, *Chem. Phys. Lett.* **1995**, *243*, 526 – 532.
[23] W. Akemann, D. Laage, P. Plaza, M. M. Martin, M. Blanchard-Desce, *J. Phys. Chem. B* **2008**, *112*, 358 – 368.
[24] E. D. Rekaï, J.-B. Baudin, L. Jullien, I. Ledoux, J. Zyss, M. Blanchard-Desce, *Chem. Eur. J.* **2001**, *7*, 4395 – 4402.
[25] M. G. Kuzyk, *J. Chem. Phys.* **2003**, *119*, 8327 – 8334.
[26] J. C. Collings, S.-Y. Poon, C. Le Droumaguet, M. Charlot, C. Katan, L.-O. Pålsson, A. Beeby, J. A. Mosely, H. M. Kaiser, D. Kaufmann, W.-Y. Wong, M. Blanchard-Desce, T. B. Marder, *Chem. Eur. J.* **2009**, *15*, 198 – 208.
[27] C. Sissa, V. Parthasarathy, D. Drouin-Kucma, M. H. V. Werts, M. Blanchard-Desce, F. Terenziani, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11715 – 11727.
[28] H. M. Kim, M. S. Seo, S.-J. Jeon, B. R. Cho, *Chem. Commun.* **2009**, 7422 – 7424.
[29] F. Terenziani, M. Morone, S. Gmouh, M. Blanchard-Desce, *ChemPhysChem* **2006**, *7*, 685 – 696.
[30] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991 – 1024.
[31] C. Xu, W. W. Webb, *J. Opt. Soc. Am. B* **1996**, *13*, 481 – 491.
[32] M. H. V. Werts, N. Nerambourg, D. Pélégry, Y. Le Grand, M. Blanchard-Desce, *Photochem. Photobiol. Sci.* **2005**, *4*, 531 – 538.
[33] M. A. Albota, C. Xu , W. W. Webb, *Appl. Opt.* **1998**, *37*, 7352 – 7356.
[34] C. Katan, S. Tretiak, M. H. V. Werts, A. J. Bain, R. J. Marsh, N. Leonczek, N. Nicolaou, E. Badaeva, O. Mongin, M. Blanchard-Desce, *J. Phys. Chem. B* **2007**, *111*, 9468 – 9483.

Received: September 20, 2010
Published online: February 16, 2011

