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Novel Fluorophores: Efficient Synthesis and Photophysical Properties

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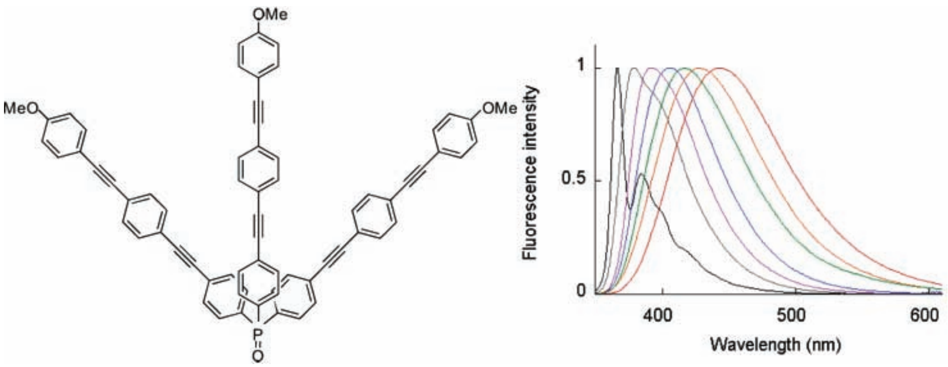
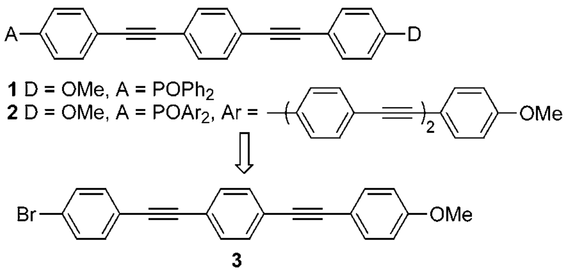
ABSTRACT



The synthesis of new donor–acceptor acetylene-bridged compounds was realized via organophosphorus reactions and Sonogashira couplings. These systems exhibit high fluorescence quantum yields, and excitation induces very efficient charge redistribution in the molecules.

The design of new organic fluorescent molecules has attracted increasing attention for their potential optical[1] and sensing[2] applications. The structural diversities of fluorophores offer widespread opportunities in many fields, but the photophysical properties always need to be improved and adjusted. In this context, poly(phenylene ethynylenes) and other arylethynyl fluorophores are very attractive because of their electron-transport abilities and their intense fluorescence emission.[3] A series of push−pull chromophores (D−π−A) containing a polyphenylethynyl unit as a conjugated bridge were already studied (Scheme 1).[4] In these systems, photoexcitation induces substantial charge separation as evidenced by the large solvatochromic shift observed on emission spectra. The nonlinear properties of some of those

Scheme 1



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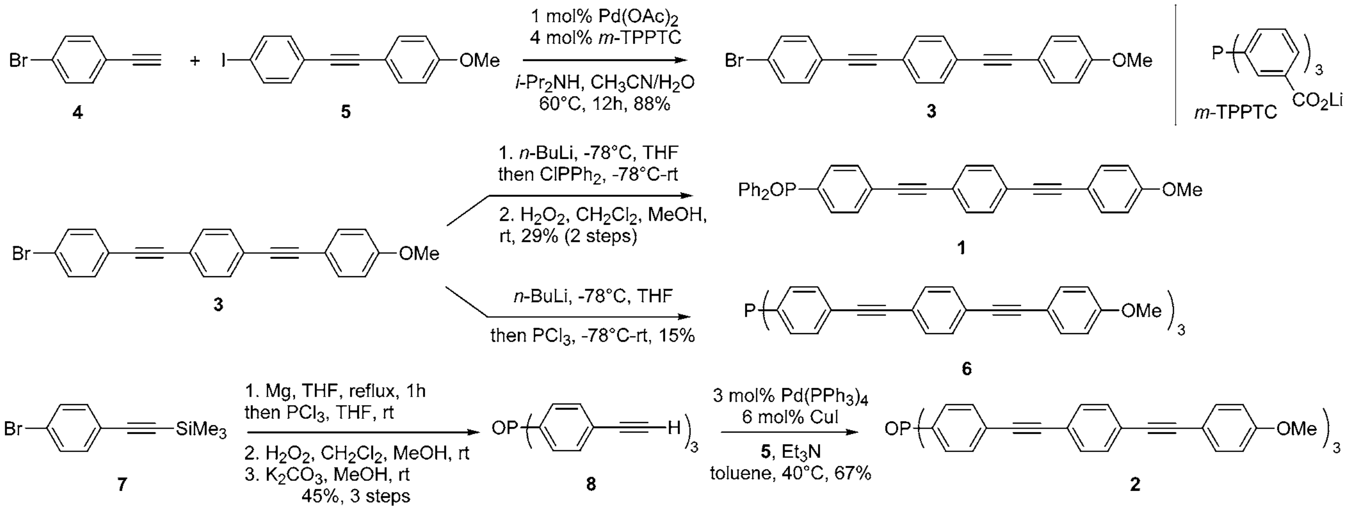
Scheme 2



related compounds were already investigated.[5] In our continuing search for novel fluorescent molecular sensors for alkaline cations,[6,7] we focused on the design of new photoinduced charge-transfer (PCT) fluorophores. We turned our attention to phosphine oxide derivatives that seem very promising for cation complexation.[8] Taking into account the high fluorescence quantum yield of polyphenylacetylene and the PCT character of triphenylphosphine oxide substituted by a donor group,[9] we envisaged preparing new polyphenyl acetylene phosphine oxides bearing a methoxy donor group (Scheme 1). In this report, we wish to disclose our preliminary results in the first synthesis and the photophysical properties of these new fluorophores.

A general procedure for preparing substituted arylphosphine uses organometallic derivatives and phosphorus chloride. On the basis of our recent synthesis of water-soluble phosphine,[10] we envisaged a common strategy for trisubstituted phosphine oxide derivatives bearing one or three triphenylacetylene moieties (Scheme 1). Phosphine oxides **1** and **2** were expected to be delivered by means of an organophosphorus reaction either with phosphorus trichloride or chlorodiphenylphosphine followed by an oxidation reaction starting from the bromophenylacetylene **3**.

The synthesis of the bromo compound **3** was recently described in the literature starting from 1,4-diiodobenzene via two Pd-catalyzed cross-couplings.[11] We have found that the second Pd-catalyzed Sonogashira coupling could be improved in the presence of a water-soluble catalyst (Scheme 2). The new water-soluble carboxylated ligand *m*-TPPTC[10,12] combined with 1 mol % Pd(OAc)$_2$ catalyst indeed afforded the clean and efficient reaction of 4-bromophenylacetylene **4** with iodide compound **5** in 88% yield. The phosphorylation was then investigated using chlorodiphenylphosphine and phosphorus trichloride, respectively. The lithium−bromide exchange was conducted in the presence of *n*-BuLi at −78 °C in THF, and the reaction mixture was reacted with ClPPh$_2$, leading to the corresponding phosphine, which was directly oxidized in 29% overall yield. In the same manner, the reaction of the lithiated anion with PCl$_3$ afforded the phosphine **6**, despite a low yield of 15%. Attempts to increase the yields were unfruitful, probably due to the high polarity and therefore the low solubility of bromide **3**. Anticipating that phosphine oxide **2** may exhibit higher fluorescent properties, we turned our attention to an alternate preparation based on the synthesis of the key intermediate **8** (Scheme 2). The phosphorylation using the Grignard derived from the commercially available 4-bromo-trimethylsilylphenylacetylene **7**, followed by phosphorus oxidation and desilylation reaction, led to the desired adduct **8** in 45% overall yield. The Sonogashira coupling of the phosphine oxide **8** with the iodide **5** gave the corresponding triarylphosphine oxide **2** in 67% isolated yield. UV absorption and steady-state and time-resolved fluorescence emission properties of these new fluorophores were then investigated at room temperature in order to obtain a full characterization of the

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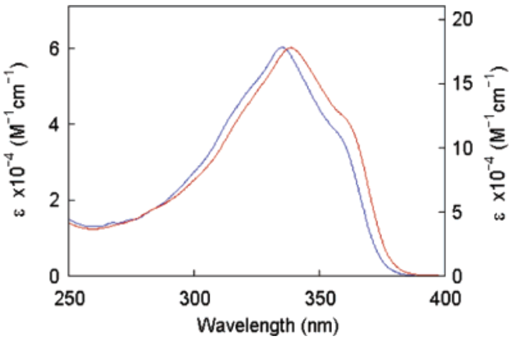

Figure 1. Absorption spectra of **1** (blue) and **2** (red) in $CHCl_3$. For comparison, right and left ordinate scales for molar extinction coefficients have a ratio equal to 3.

photophysical behaviors and to evaluate the photoinduced charge transfer (PCT) that occurs in these molecules.

As shown in Figure 1 and Table 1, the new fluorophores exhibit an intense absorption band in the UV region. After normalization to the same number of chromophores, the molar absorption coefficients at the wavelength of maximal absorption are similar for **1** and **2**. The absorption of **2** is only slightly red-shifted with regard to the corresponding band of **1**, which reveals a weak interaction between the chromophores in the ground state for **2**.[13]

Table 1. Photophysical Data for **1** and **2**

	solvent	λ_{abs} (nm), ϵ^a	λ_{em} (nm)	$\Phi_F{}^b$	τ (ns)
1	cyclohex	333	364	0.77	0.63
1	dioxane	333	374	0.97	0.73
1	$CHCl_3$	335, 5.9	388	0.76	0.78
1	CH_2Cl_2	334, 6.1	402	0.78	0.87
1	DMSO	336	434	0.75	1.17
1	EtOH	333	412	0.81	1.03^c
1	CH_3CN	331	422	0.94	1.13
2	cyclohex	335	366	0.78	0.58
2	dioxane	336	379	0.89	0.69
2	$CHCl_3$	338, 17.7	392	0.77	0.74
2	CH_2Cl_2	338, 18.0	406	0.73	0.85
2	DMSO	338	443	0.71	1.24
2	EtOH	336	418	0.86	1.02^c
2	CH_3CN	334	428	0.79	1.14

[a] Units = 10^4 M^{-1} cm^{-1}. [b] Fluorescence quantum yield with a 10% random error. [c] Additional decay time of 40 ps (fractional intensity f_i = 1−2%) was found.

As expected, **1** and **2** are strongly fluorescent (Φ_F varies from 0.7 to 0.9) in the 350−600 nm region (Figures 2A and 2B). A large Stokes shift (up to 7000 cm^{-1} for **2** in DMSO) and the unresolved vibronic structure of the fluorescence spectrum observed for **1** and **2** in a polar solvent suggest the formation of an intramolecular charge transition. The Stokes shifts, obtained for **1** and **2** in different solvents, can be used to evaluate the difference in dipole moments between the ground and the excited states ($\mu_e - \mu_g$) by using the Lippert−Mataga equation:[14]

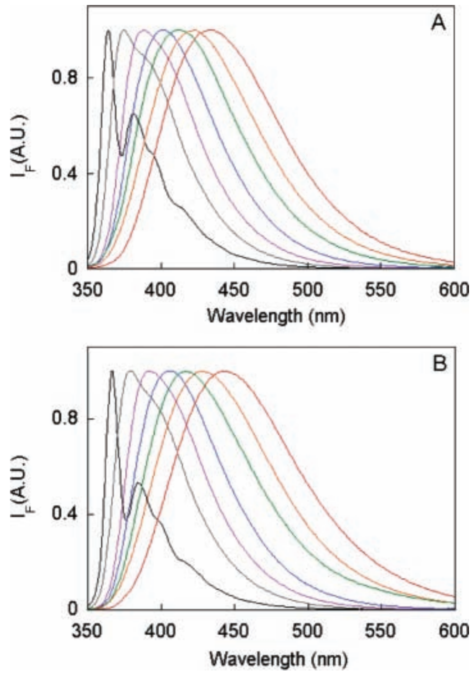

Figure 2. Corrected fluorescence spectra of **1** (Panel A) and **2** (Panel B) in various solvents (cyclohexane, black; dioxane, gray; $CHCl_3$, purple; CH_2Cl_2, blue; DMSO, red; CH_3CN, orange; EtOH, green). Spectra are normalized to the same height at the maximum.

$$\nu_a - \nu_f = \frac{2}{hca^3}(\mu_e - \mu_g)^2 \Delta f + \text{constant} \qquad (1)$$

where ν_a and ν_f are the frequencies of the absorption and fluorescence maximum, respectively, *h* is Planck's constant, *c* is the velocity of light, *a* is the radius of the cavity in which the solutes reside, and Δf is the orientation polarizability defined as:

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

where ϵ is the static dielectric constant of the solvent, and *n* is the optical refractive index of the solvent.

Taking the Onsager cavity of the fluorophore **1** to be 9 Å, which is half the length of the long axis of the molecule, the enhancement of the dipole moment was found to be about 30.5 D. Since the dipole moment in the ground state was evaluated to be 4.9 D using a quantum semiempirical PM3 model, the dipole moment in the excited state may be larger than 35 D. Such a value points out a significant separation of the charges upon excitation (~40% of an electron being

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transferred) which is in accordance with the dimethylamino-cyano-diphenylacetylene behaviors.[15,16] The observed Stokes shifts for **2**, and all of the photophysical parameters mentioned in Table 1, are comparable to those for **1**, as in the case of dimethylamino-substituted triphenylphosphine oxide derivatives.[10] These observations suggest that interactions within the trimer molecule are relatively weak and show that excitation energy is more likely to be localized on only one chromophore in the case of **2**. Such a property is fully compatible with the work of Goodson et al.[17] The Onsager radius of the fluorophore **2** is identical to the one calculated for **1** ($a = 9$ Å), and consequently the dipole moment of the excited fluorophore is also around 35 D. The other two phenylacetylene fluorophores contained in the trimer molecule **2** seem to have no significant influence on the acceptor character of the phosphine oxide function.

Fluorescence decays were measured by the time-correlated single-photon counting method with a picosecond laser excitation. For **1** and **2**, in all solvents except ethanol, a monoexponential behavior was found. An example of the fluorescence decay obtained for **2** in dichloromethane is given in Figure 3. Furthermore, the excitation spectra were independent of the selected emission wavelength and very similar to the absorption spectrum. Those results suggest the presence of only one emitting species, in contrast to the observation of Garcia−Garibay,[18] and therefore reinforce the observations made by Beeby et al. on 1,4-bis-(phenylethynyl)benzene.[19] We did not observe any evidence of different rotamers for **1** and **2**.

For **1** and **2** in ethanol, the observed minor decay component ($f_\text{i} = 1-2\%$) with a decay time of 40 ± 25 ps (shortest time scale available on our instrumentation) was interpreted as a dynamic Stokes shift with a decay time corresponding to the characteristic time of solvent relaxation.[20] In contrast with the fluorescence quantum yield, which slightly depends on the polarity of the solvent, the fluorescence lifetime increases substantially by increasing the solvent polarity.

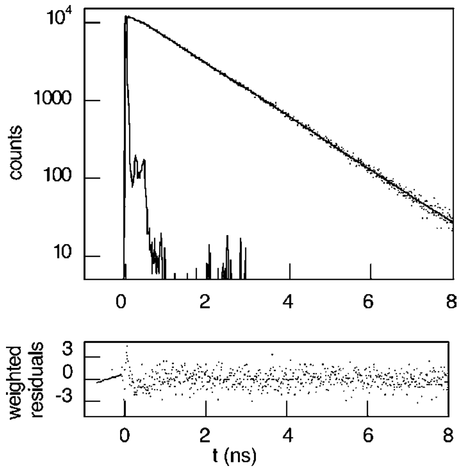

Figure 3. Fluorescence decay data of compound **2** in CH_3CN by excitation at $\lambda_{\text{exc}} = 330$ nm and collected emission $\lambda_{\text{em}} > 355$ nm. Experimental data (points) and best fit (solid line) were obtained by considering a single exponential. The obtained weighted residual is plotted in the bottom panel.

In summary, we have prepared two novel polyphenyl acetylene phosphine oxides bearing a methoxy group via organophosphorus reactions and efficient Pd-catalyzed Sonogashira couplings. These systems exhibit high fluorescence quantum yields and excitation inducing very efficient charge redistribution in the molecules. These novel fluorophores open new opportunities for the conception of new fluorescent molecular sensors. Further studies are currently underway for the synthesis of analogues and probes and the evaluation of photophysical properties and will be reported in due course.

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Supporting Information Available: General experimental procedures for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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