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New 4,4′-oligophenylenevinylene functionalized-[2,2′]-bipyridyl chromophores: synthesis, optical and thermal properties

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Abstract—The synthesis and characterization of new bipyridyl-based chromophores featuring extended oligophenylenevinylene π-conjugated backbones are reported. Their absorption and emission properties as well as their thermal stabilities are discussed in comparison to those of the parent ligand.

Organic molecules bearing extended π-conjugated systems are attracting much attention for their properties in the field of molecular electronics[1] and photonics.[2] In particular, oligophenylenevinylene derivatives (OPV) have been extensively investigated in regard to applications in the fields of photo- and electroluminescence,[3] photovoltaism,[4] or nonlinear optics (NLO).[5] In this context, our group has been involved in the design of 4,4′-disubstituted-[2,2′]-bipyridines as fluorophores and precursors to molecular,[6a,b] macromolecular[6c] and supramolecular[6d] metallo-octupoles for second order nonlinear optics. From the wide range of 4,4′-π-conjugated bipyridyl ligands already prepared,[7] such as 4,4′-bis(dibutylaminostyryl)-[2,2′]-bipyridine **1**, we have previously shown how simple modification of the π linker enables the generation of tunable chromophores and fluorophores. Continuing our effort to probe the structural factors that could improve the optical and nonlinear optical properties of π-conjugated bipyridyl ligands and complexes, we report herein the synthesis of new bipyridines featuring extended oligophenylenevinylene π-conjugated backbones (OPV-bpy) **2**–**3** which are the styrene-based homologues of **1** (Chart 1). Their optical properties (absorption and emission) as well as their thermal stability will be discussed with regard to those of the parent ligand **1**.

Several methodologies were tested for the preparation of OPV-bpy **2**–**3**. The first attempts, involving a classical Knoevenagel condensation between 4,4′-dimethyl-[2,2′]-bipyridine and the corresponding aldehydes, in the presence of lithium diisopropylamide or potassium-*tert*-butoxide, failed.[7] A Heck cross-coupling reaction between 4,4′-bis-vinyl-[2,2′]-bipyridine[8] and 4-dibutylamino-4′-bromostilbene was also carried out by analogy with the preparation of analogous push–pull OPV-pyridines,[9] but in our case no reaction occurred. Further investigations involving Heck cross-coupling between 4,4′-bis(bromostyryl)-[2,2′]-bipyridine[10] and *p*-dibutylaminostyrene under various conditions always gave mixtures of **2** and the corresponding monofunctionalized derivative which could not be separated by crystallization or chromatography. Finally, the synthesis of OPV-bpy's **2**–**3** was achieved by means of a double Wadsworth–Emmons reaction, as depicted in Scheme 1. The preparation of the aldehyde precursors **7**[11] and **11** was carried out using different routes. Reaction of 4-bromobenzyl bromide **4** in refluxing $P(OEt)_3$ gave the corresponding phosphonate **5**; subsequent Wittig-type reaction with *p*-dibutylaminobenzaldehyde resulted in the formation of the stilbene **6**. Further halogen–lithium exchange, followed by quenching of the lithiated intermediate with dimethylformamide led to the formation of the desired aldehyde **7** in 36% overall yield after purification by column chromatography. The use of a similar methodology failed for the preparation of the "styrylogous" compound **11**. However, this could be prepared in 21% overall yield by using an alternative four-step

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Keywords: bipyridines; chromophores; fluorophores.

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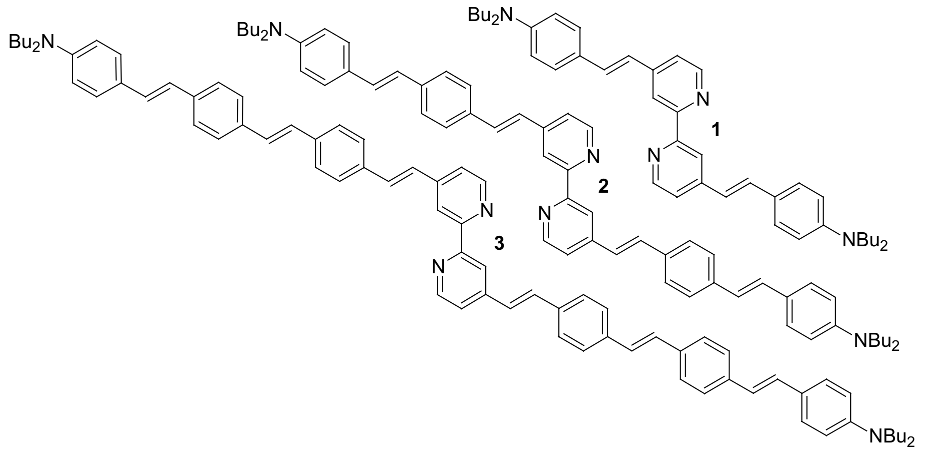
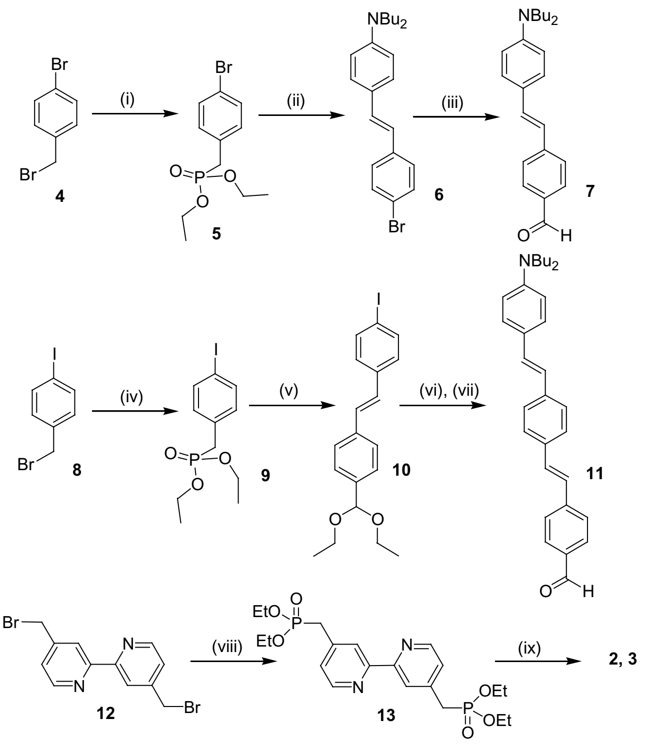


Chart 1.



Scheme 1. Reagents and conditions: (i) $P(OEt)_3$, Δ, 17 h (85%); (ii) *p*-dibutylaminobenzaldehyde, NaH, THF, Δ, 3 h (88%); (iii) ^{n}BuLi, Et_2O, −10 °C followed by DMF, −10 °C, 1 h (48%); (iv) $P(OEt)_3$, Δ, 17 h (83%); (v) terephthalaldehyde monodiacetal, NaH, THF, Δ, 3 h (98%); (vi) *p*-dibutylaminostyrene, P(*o*-tolyl)$_3$, $Pd(OAc)_2$ cat., NEt_3:DMF (2:1), Δ, 17 h (48%); (vii) HCl (6 N), EtOH, Δ, 12 h (54%); (viii) $P(OEt)_3$, $CHCl_3$, Δ, 3 h (93%); (ix) **7**, **11**, ^{t}BuOK, THF, rt, 3 h (76–72%).

synthesis.[12] The key step of this synthesis was the Heck cross-coupling reaction between the iodo-stilbene monodiethylacetal derivative **10** and *p*-dibutylaminostyrene in the presence of a catalytic amount of palladium acetate and tris-*o*-tolylphosphine in NEt_3–DMF. It is worth noting that both aldehydes **7** and **11** were obtained selectively as their *E*-isomer as shown by the $^3J_{H–H}$ coupling constant of ca. 16 Hz between all vinylic protons.

4,4′-Bis(phosphonate)-[2,2′]-bipyridine **13** was synthesized quantitatively by means of an Arbuzov reaction from the 4,4′-bis(bromomethyl)-[2,2′]-bipyridine precursor **12**.[13] Finally, treatment of **13** with aldehydes **7** and **11** under normal Wittig conditions afforded the desired OPV-bpy's **2**–**3** in excellent yields after purification by recrystallization (76% and 72%, respectively).[14] Bipyridine **2** is soluble in common organic solvents (CH_2Cl_2, THF, …) and was characterized by ^{1}H, ^{13}C NMR, absorption and emission spectroscopies, high resolution mass spectrometry and gave satisfactory elemental analysis. The NMR data were in agreement with the proposed structure; in particular the *E* configuration of all double bonds was established unambiguously on the basis of the $^3J_{H–H}$ vinylic coupling constant of ca. 16 Hz. Conversely, the high insolubility of **3** bearing the most extended conjugated chain (up to six styryl moieties),[15] prevented its complete spectroscopic characterization.

Bipyridines **1**–**3** exhibit intense structureless charge transfer (ICT) transitions in the visible range (Table 1 and Fig. 1). The extension of conjugation results in a moderate bathochromic shift in the case of the first homologation ($\Delta\lambda_{max}$ (**2** vs **1**) = 19 nm, but an additional red shift ($\Delta\lambda_{max}$ (**3** vs **2**) = 1 nm) is not observed for the second homologation. Such saturation in λ_{max} has already been observed for other push–pull OPV derivatives and can be explained by a decrease of the charge transfer character with an increase of the conjugation length.[5,16] Interestingly, the λ_{max} saturation limit occurs at ca. 421 nm ($\nu_{sat} = 23{,}753\,cm^{-1}$), a value in good agreement with the convergence limit ($\nu_\infty = 23{,}231$ cm^{-1}) reported by Meier and co-workers in the case of a four push–pull OPV series bearing a dialkylamino donor group and various acceptor fragments (NO_2, CHO, CN, H).[16a] In addition the absorption half bandwidth ($\nu_{1/2} = 4280$, 5048, 6039 cm^{-1} for **1**, **2**, **3**, respectively)

Table 1. Absorption, emission properties and thermal stability of OPV-bpy **1**–**3**

Compound	λ_{max} (nm)	ε ($L\,mol^{-1}\,cm^{-1}$)	λ_{em}[a] (nm)	Stokes shift (nm)	ϕ_F[a]	$T_{d_{5-10}}$[b] (°C)
1	401	65,000	497	96	0.23	355–380
2	420	78,000	598	178	0.70	330–360
3	421	—	630	209	—	330–385

[a] Fluorescence experiments were performed at 298 K in diluted dichloromethane solution (ca. 10^{-5}–10^{-6} $mol\,L^{-1}$).

[b] 5% and 10% weight loss temperatures.

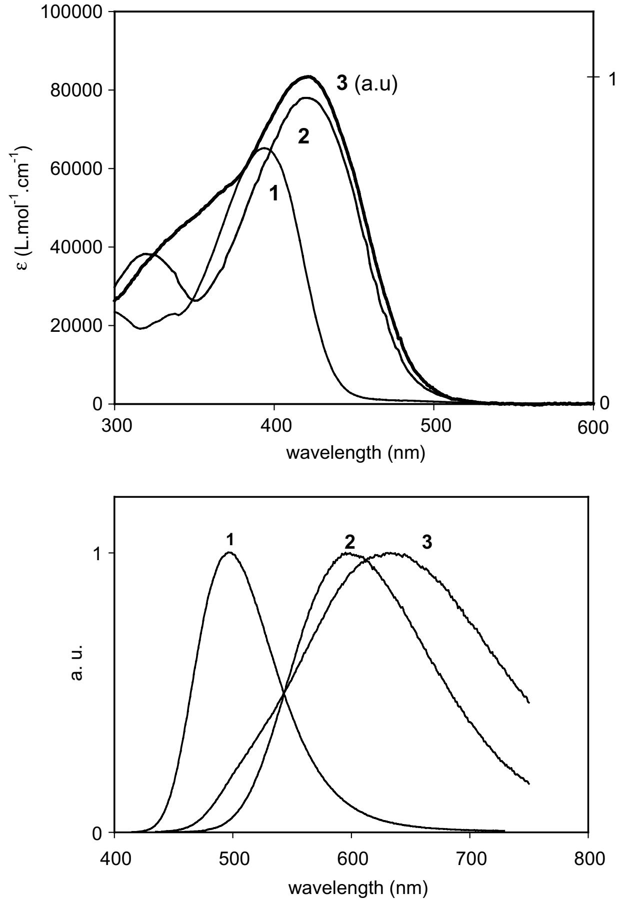


Figure 1. Absorption (top) and emission (bottom) spectra of OPV-bpy's **1**–**3** in dichloromethane solution at 298 K.

increases with the conjugation length, in agreement with an increased number of one-photon allowed excited states.[5]

Like **1**, the bis- and tris-styryl bipyridines **2** and **3** exhibit an intense structureless fluorescence band (Fig. 1). In contrast to the absorption band, a systematic bathochromic shift of the emission band is observed from **1** to **3**. The Stokes shifts are very large, ranging from 96 for **1** to 209 nm for **3** (Table 1), thus increasing as the conjugation length increases.[5] Importantly, the conjugation length also has a dramatic influence on the fluorescence quantum yield (ϕ_F) (Table 1); a threefold enhancement is observed for the 'styrylogous' derivative **2** ($\phi_F = 0.70$ vs fluorescein) compared to **1** ($\phi_F = 0.23$).

Thermal stability is one of the key requirements for practical application of organic chromophores as dopants in a polymeric or inorganic matrix. The decomposition temperatures $T_{d_{5-10}}$ corresponding to 5% and 10% weight loss, respectively, were determined by thermogravimetric analysis under nitrogen and are summarized in Table 1. In the case of the stryrylogous series **1**–**3**, the thermal stability remains very high, around 350 °C, showing that the homologation does not induce any significant decrease of the thermal stability. In a previous study,[7] we have already observed that the nature of the conjugated backbone has a dramatic influence on the T_d values, the styryl-bpy derivatives being much more stable thermally than the corresponding azo and imino compounds. Here we also show that the introduction of styryl groups in the conjugated backbone of **1** allows conservation of the molecular thermal stability. Thus, these OPV-bpy's can be considered as thermally robust chromophores with among the highest thermal stabilities reported in the literature for organic chromophores and fluorophores.[17]

To summarize, we have synthesized new bipyridine chromophores featuring oligophenylenevinylene conjugated groups. Work towards the use of these ligands for the design of octupolar bipyridyl metal complexes combining high thermal stability and large first hyperpolarizability is in progress.

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