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Donor–acceptor amphiphilic 2,2′-bipyridine chromophores: synthesis, linear optical, and thermal properties

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ABSTRACT

Two symmetrical and one unsymmetrical 'push–pull' amphiphilic 2,2′-bipyridine chromophores have been synthesized through Horner–Wordsworth–Emmons and Knoevenagel reaction mechanized synthetic protocols and characterized by spectroscopy. Linear optical properties and thermal stability of the synthesized chromophores have been investigated.

There is a considerable research interest on the electron donor–acceptor (EDA) molecules because of their widespread applications, especially in the areas of non-linear optics (NLO)[1] and optoelectronics[2] etc. 2,2′-Bipyridines are excellent chelating ligands in forming coordination complexes due to their potential metal ion binding capability.[3] The electronic blending of 2,2′-bipyridine with suitable donor groups attached to the 4- or 4,4′-positions through π-linker (transmitter), results in the construction of 4- or 4,4′-π-conjugated-2,2′-bipyridines, in which the electron drifting nature of the pyridine rings makes them archetypal examples of 'push–pull' or EDA molecules. These molecules are synthetically flexible and offer easy optical tuning (absorption, emission etc.) through variation/simple modification of their π-backbones. Since the last two decades, several research groups, especially, Bozec, Abbotto, Beer, and others have reported a number of such chromophores and interesting properties of their transition metal complexes.[4–6] Another motivating feature of these molecules is their metal ion templated macroscopic assemblies and these coordination complexes exhibit potential applications toward octupolar nonlinearity[7] and solar energy harvation.[8] Langmuir–Blodgett (LB) technique, on the other hand, is the most efficient technique for ultra-thin monolayered deposition of amphiphilic compounds with precise and accurate thickness.[9] LB films, formed from coordination complex based surfactants, are still less explored in literature. A recent publication by Bolink et al. describes dual-emitting nature of the LB films built from Ru(II) or Ir(III) complexes of amphiphilic bipyridyl compounds with other co-ligands.[10] Oligophenylenevinylene (OPV) derivatives are highly conjugated organic molecules and are often registered as organic light-emitting diodes (OLED).[2] π-conjugated-2,2′-bipyridines can also act as OLED if suitable donor groups are attached to the specified positions in the π-backbone of 2,2′-bipyridines.[11] Therefore, it would be interesting to investigate the optical properties of the LB films, fabricated from mixed-ligand coordination complexes of the appropriate transition metals, featuring both the amphiphilic and suitably functionalized bipyridine chromophores. We have recently reported the synthesis and photo-physical properties of OPV functionalized bipyridines bearing methoxy donors.[5f] In this communication, we wish to report three amphiphilic bipyridine chromophores (**TM 1–3**, see Fig. 1 for their structural representations) along with their detailed photo-physical and thermal behaviors.

The bipyridine chromophores **TM 1–3** (Fig. 1) have been obtained in gram quantities (2–3 g) through condensation of suitable bipyridine precursors and functional benzaldehydes. The C_{10} and C_{14} alkyl chain containing aldehydes (**Ald 1–2**) have been synthesized using the reaction protocol as described in Scheme 1. In the first step, the diol (**1**) has been mono-brominated using an analogous procedure reported by Chong et al.[12] The product (**1a**) has then been converted to its tetrahydropyranyl ether (THP) by overnight stirring of a THF solution of **1a** containing 1.5 equiv of 3,4-dihydro-2*H*-pyran (DHP) and 5 mol % of *p*-toluenesulfonic acid (PTSA). The successive N-alkylation of *N*-methyl aniline (**2**) has then been performed with **1b** in refluxing THF. After an acid mediated cleavage of the OTHP functionality, the hydroxy containing *N*,*N*-dialkyl aniline **2a** has been obtained in a moderate yield

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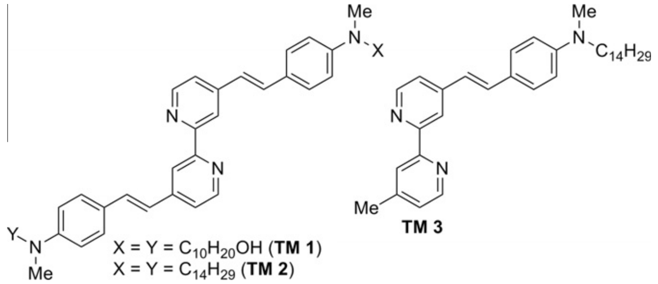


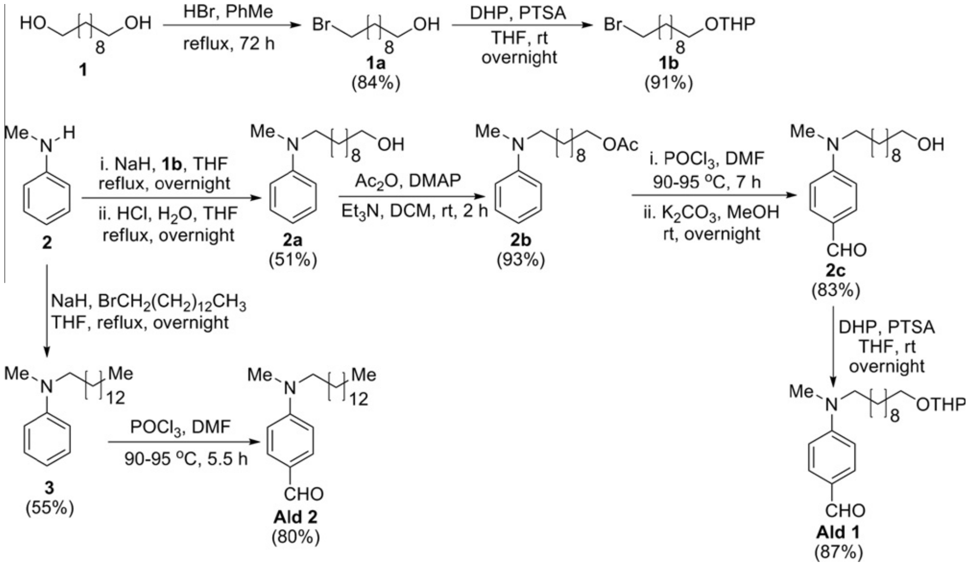
Figure 1. Molecular structure of the synthesized π-conjugated amphiphilic bipyridine chromophores (**TM 1–3**).

(51%). The hydroxy group has then been almost quantitatively protected by acetyl functionalization in dichloromethane using acetic anhydride in presence of catalytic amount (10 mol %) of 4-dimethylamino pyridine (DMAP). The next step involves the classical Vilsmeier–Haack formylation of the dialkyl aniline **2b** followed by cleavage of the acetyl group to form the aldehyde **2c**, the hydroxy group of which has then been converted to its THP ether (**Ald 1**). The synthesis of the aldehyde **Ald 2** involves an analogous synthetic route as described for the synthesis of **Ald 1** (Scheme 1).

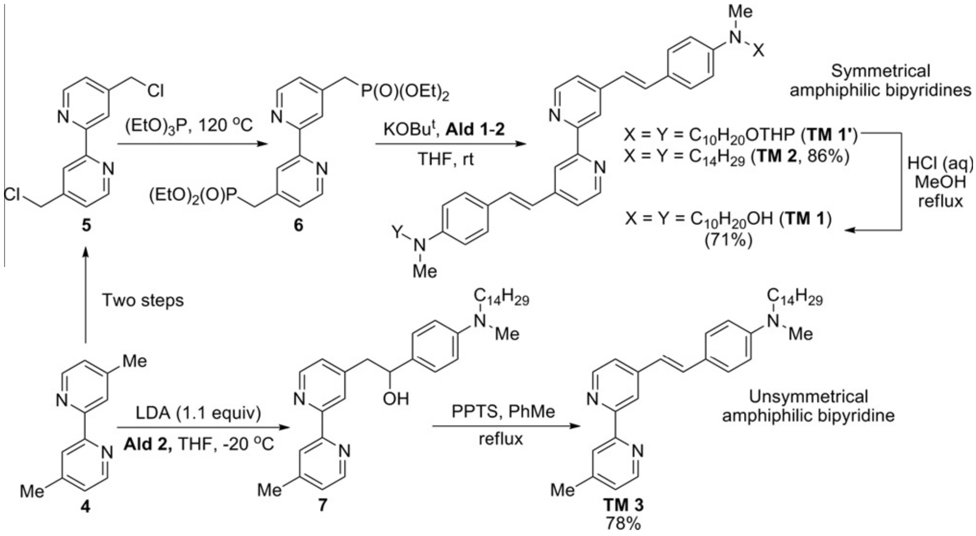
The π-functionalized-2,2′-bipyridine compounds (**TM 1–3**) have been synthesized following two different synthetic protocols viz. (i) Knoevenagel type condensation between 4,4′-dimethyl-2,2′-bipyridine (**4**) and the appropriate aldehyde, and (ii) Horner–Wordsworth–Emmons (HWE) reaction of the bis-phosphonate precursor (**6**) with suitable aldehydes. The resulting bipyridine chromophores (**TM 1–3**) are sufficiently soluble in common organic solvents thereby allowing easy chromatographic purification. The tricky step of the synthesis is the halogenation of 4,4′-dimethyl-2,2′-bipyridine (**4**). Attempt to prepare the brominated precursor 4,4′-bis-bromomethyl-2,2′-bipyridine by a radical mechanized bromination of 4,4′-dimethyl-2,2′-bipyridine (**4**) with *N*-bromosuccinimide (NBS) in refluxing CCl_4 (in presence of radical initiator benzoyl peroxide or AIBN) has resulted in multiple number of products (closely spaced multiple spots in TLC) from where, chromatographic separation of the desired product (4,4′-bis-bromomethyl-2,2′-bipyridine) was difficult. This is in accord with some literature reports, which comment about poorer performance of this reaction,[13] although there are some reports that document even selective bromination (mono- or di-) of **4** under similar reaction condition.[14] However, in the present case, the chlorinated analog, 4,4′-bis-chloromethyl-2,2′-bipyridine (**5**) has been used that has been synthesized following an efficient procedure described by Fraser and co-workers.[15] An Arbuzov reaction of **5** with triethylphosphite has converted it to the corresponding bis-phosphonate (**6**). Finally, the HWE condensations between **6** and the appropriate functional benzaldehydes (**Ald 1–2**) at room temperature have afforded the symmetrically substituted bipyridine chromophores (**TM 1–2**) in good yields (Scheme 2). **TM 1**, containing hydroxy functionalization has required an acid-hydrolysis of its corresponding THP ether (**TM 1′**). The dissymmetrically substituted bipyridine chromophore (**TM 3**) has been synthesized via controlled Knoevenagel type condensation between mono-deprotonated **4** and **Ald 2** followed by dehydration of the resulting mono-ol (**7**) in presence of catalytic amount of pyridinium-*p*-toluene-sulfonate (PPTS) in refluxing toluene.

The synthesized chromophores have been characterized by spectroscopy including successful elemental analyses.[16–18] The conformation of the vinylic bonds of **TM 1–3** have unequivocally been designated as *E* on the basis of J_{HH} vinylic coupling constant (ca. 16 Hz).

The steady state absorption and emission properties of the π-conjugated bipyridines, **TM 1–3**, have been investigated in dichloromethane at room temperature. The relevant spectra have been presented in Figure 2 and the concerned optical data have been tabularized in Table 1. The absorption spectra of the chromophores, **TM 1–3** have been characterized by a broad structureless absorption band in the near-visible region (λ_{max} = 390–395 nm). This band unambiguously corresponds to the intra-ligand charge transfer (ICT) from the dialkylamino donors to the pyridinic acceptor subunits and this is in fact evident from the following observations: (i) the absorption is broad and rather intense ($\varepsilon \approx$35,000–42,000 $L{\cdot}cm^{-1}{\cdot}mol^{-1}$), (ii) the position of the band maxima is sensitive to the polarity of the fluid medium (vide Table 2). The presence of the ICT band clearly demonstrates the 'push–pull' electronic grouping between the donor and acceptor subunits of the title chromophores. The molar absorptivity of the ICT band in the spectrum of **TM 3** is relatively lower than that of the other two compounds, presumably due to the presence of only one donor sub-chromophore in **TM 3** compared to two in **TM 1** and **TM 2**. However, the position of the concerned ICT band remains almost



Scheme 1. Synthesis of the dialkylamino benzaldehydes.



Scheme 2. Synthetic routes to obtain the π-conjugated bipyridine chromophores (**TM 1**–**3**).

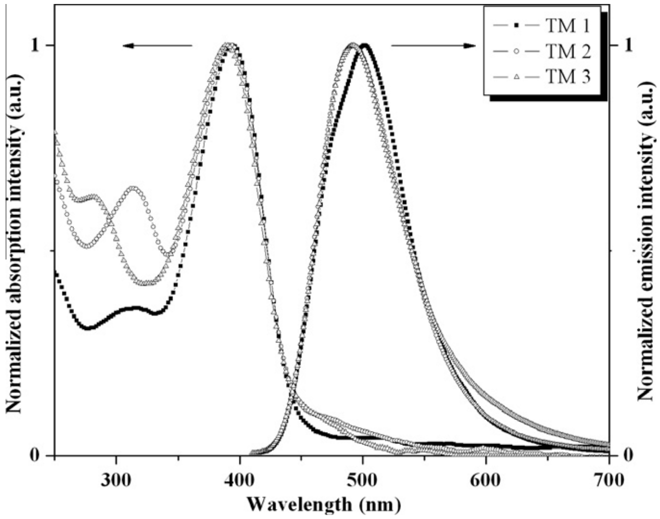


Figure 2. Normalized steady-state electronic absorption and emission spectra of the compounds **TM 1**–**3** in dichloromethane at 298 K. Concentration of the solutions has been adjusted such that OD ≈0.05 in the relevant absorption spectra. Emission spectra have been recorded after exciting the solutions at the corresponding lowest energy absorption band maxima.

Table 1

Summary of the linear optical (dichloromethane, 298 K) and thermal data for **TM 1**–**3**

	λ_{abs} (nm)	ε (L·cm^{-1}·mol^{-1})	λ_{em} (nm)	Φ_{em}[a]	Td$_{10}$[b] (°C)
TM 1	395	42,274	495	0.138	375
	250	20,685			
TM 2	393	43,585	493	0.135	367
	320	25,142			
	247	24,228			
TM 3	390	35,114	490	0.096	389
	285	23,742			
	246	26,257			

[a] Measured using quinine sulfate as the reference in 1 N H_2SO_4 (Φ_{em} = 0.546).

[b] 10% weight loss temperature.

Table 2

Summary of the linear optical data for the compounds **TM 1**–**3** in various solvents at 298 K, λ (nm)

Solvent	TM 1		TM 2		TM 3	
	λ_{max}	λ_{em}	λ_{max}	λ_{em}	λ_{max}	λ_{em}
Hexane	–	–	380	428	372	426
PhMe	385	445	390	440	382	445
THF	391	476	390	477	385	475
EtOAc	386	476	389	473	381	476
DCM	395	495	393	493	390	490
DMF	400	524	397	524	392	518
MeCN	385	521	383	515	386	521
MeOH	398	530	390	535	392	533

invariant in the absorption spectra of all the compounds. The chromophores, **TM 1**–**3**, fluoresce in fluid medium at room temperature (see Fig. 2 and Table 1). Origination of the emission bands in all the cases has been crosschecked by comparing the corresponding excitation spectra with the original absorption spectra of the respective compounds. The fluorescent spectra of the chromophores in DCM exhibit broad structureless blue emission (λ_{em} = 490–495 nm) with ca. 100 nm Stokes' shift between the emission and the lowest energy absorption maxima. The photoluminescent quantum yields of these compounds have been measured in DCM using quinine sulfate as the reference substance[19] in 1 N H_2SO_4 (298 K) and have been found to be 0.138, 0.135 and 0.096 for the compounds **TM 1**–**3**, respectively. Thus, it is obvious that introduction of the hydroxy functionality has not induced any significant change in the electronic properties of the bipyridine chromophores. This observation is consistent with the similar chromophores reported by Bozec and coworkers.[4a]

Solvatochromism has been observed for all the title bipyridine chromophores (**TM 1**–**3**). The corresponding optical data have been summarized in Table 2 and the relevant spectra have been presented in the section of Supplementary data. Broad structureless absorption and emission bands are featured in all the solvents, except in hexane, which exhibits structured bands. An irregular trend in the position of the absorption and emission band maxima is observed in the Reichardt's $E_T(30)$ solvent polarity scale (see Fig. 3).[20] However, Stokes' shift of the absorption and emission maxima evidently demonstrates the polarity-dependent nature of the ground and the excited electronic states of the relevant chromophores (**TM 1**–**3**). Compared to the absorption spectra, the effect of medium on the position and/or shape of the emission bands in the corresponding fluorescent spectra have been found to be profound. The change in dipole moment on electronic excitation of the chromophores is calculated using the Lippert–Mataga equation[21] and

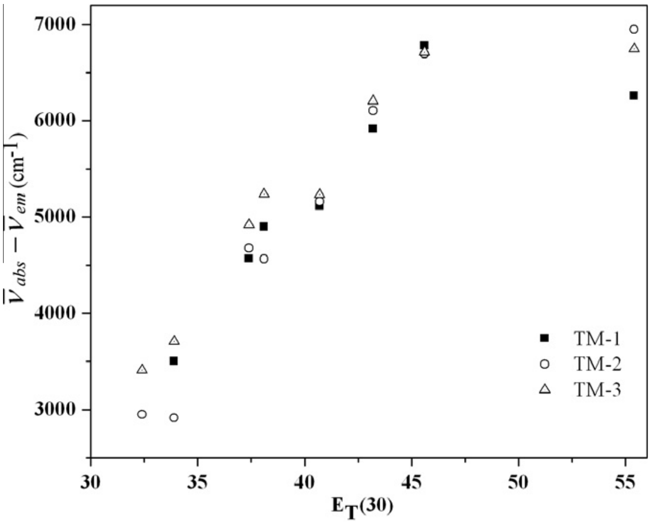


Figure 3. Variation of Stokes' shift ($\bar{\nu}_{abs} - \bar{\nu}_{em}$) of **TM 1–3** with solvent polarity parameter $E_T(30)$. The absorption and emission intensities have been measured at 298 K. Concentration of the solutions have been adjusted such that OD ≈0.05. All the excitations have been performed at the lowest energy absorption maxima. The solvents are: hexane (32.4), toluene (33.9), THF (37.4), EtOAc (38.1), DCM (40.7), DMF (43.2), MeCN (45.6), MeOH (55.4). Values in the parenthesis indicate the $E_T(30)$ values of the solvents.[20]

are estimated to be around 2.63 D, 3.20 D, and 1.27 D for **TM 1–3**, respectively (see Supplementary data).

The spectroscopic properties of the synthesized chromophores, **TM 1–3**, are found to remain unchanged over prolonged storage in air, as indicated by the NMR and UV–visible spectroscopy, revealing their chemical inertness toward air or moisture. Thermo-gravimetric analyses have been performed on the compounds **TM 1–3** under nitrogen and the respective thermogravimetric plots (see Supplementary data) exhibit high thermal stability of these chromophores. The thermal decomposition temperature of these compounds (10% weight loss temperature) has been reported in Table 1. These values are effectively higher indicating thermal robustness of these chromophores.

In conclusion, three amphiphilic bipyridine chromophores have been synthesized using appropriate reaction protocols and their optical and thermal properties have been demonstrated. The position of the absorption or emission band maxima is not found to be dependent on the alkyl chain lengths. The optical properties of LB films based on the amphiphilic and OPV mixed ligand coordination complex surfactants will be reported in near future.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.120.

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16. *Characterization data for* **TM 1**: This compound was obtained as a yellow solid after acid-hydrolysis of the chromatographed Horner–Wordsworth–Emmons product **TM 1′**. Yield: 71%; mp: 122 °C (DTA); IR (KBr, cm^{-1}): 3371.87 (O–H), 2922.42–569.05 (multiple bands); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.62 (d, J = 4 Hz, 2H), 8.48 (s, 2H), 7.45 (d, J = 8 Hz, 4H), 7.41 (d, J = 16 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 6.91 (d, J = 16 Hz, 2H), 6.69 (d, J = 8 Hz, 4H), 3.65 (t, 4H, –CH_2–OH), 3.35 (t, 4H, –N–CH_2–), 2.99 (s, 6H, –N–CH_3), 1.59–1.55 (unresolved, 8H, –N–CH$_2$–CH_2–, –CH_2–CH$_2$–OH), 1.30 (unresolved, 28H, –CH_2–); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 156.4, 149.6, 149.3, 146.8, 133.6, 128.5, 123.8, 121.0, 120.5, 117.9, 111.8, 63.0, 52.6, 38.3, 32.8, 29.5, 27.1, 26.8, 25.8; LC–MS (positive mode) *m*/*z*: 731 (M+H)$^+$; Anal. Calcd for. $C_{48}H_{66}N_4O_2$ (730.52): C, 78.86; H, 9.10; N, 7.66%. Found: C, 78.83; H, 9.06; N, 7.71%.
17. *Characterization data for* **TM 2**: Yellow solid; yield: 86%; mp: 110 °C (DTA); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.63 (d, J = 4 Hz, 2H), 8.49 (s, 2H), 7.46–7.35 (m, 10H), 6.91 (d, J = 16 Hz, 2H), 6.69 (d, J = 8 Hz, 4H), 3.35 (t, 4H, –N–CH_2–), 3.02 (s, 6H, –N–CH_3), 1.60 (unresolved, 4H, –N–CH$_2$–CH_2–), 1.32 (unresolved, 48H, –CH_2–), 0.90–0.87 (unresolved, 6H, –CH$_2$–CH_3); ^{13}C NMR (100 MHz, CDCl$_3$):

δ = 156.4, 149.6, 149.3, 146.8, 133.7, 128.5, 123.9, 121.0, 120.5, 117.9, 111.8, 52.6, 38.4, 32.0, 29.6, 29.4, 27.2, 26.8, 22.7, 14.2; LC–MS (positive mode) *m*/*z*: 812 (M+H)$^+$; Anal. Calcd for. $C_{56}H_{82}N_4$ (810.65): C, 82.91; H, 10.19; N, 6.91%. Found: C, 82.89; H, 10.16; N, 6.95%.

18. *Characterization data for* **TM 3**: Yellow solid; yield: 78%; mp: 124 °C (DTA). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 4 Hz, 2H), 8.46 (s, 1H), 8.25 (s, 1H), 7.45 (d, *J* = 8 Hz, 2H), 7.39 (d, *J* = 16 Hz, 1H), 7.34 (d, *J* = 4 Hz, 1H), 7.15 (d, *J* = 4 Hz, 1H), 6.90 (d, *J* = 16 Hz, 1H), 6.68 (d, *J* = 8 Hz, 2H), 3.35 (t, 2H, –N–CH_2–), 2.98 (s, 3H, –N–*Me*), 2.45 (s, 3H, 4–py–*Me*), 1.59 (unresolved, 2H, –N–CH_2–CH_2–), 1.27 (unresolved, 22H, –CH_2–), 0.88 (t, 3H, –CH_2–*Me*); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 156.4, 156.2, 149.6, 149.3, 148.9, 148.1, 146.8, 133.6, 128.5, 124.7, 123.8, 122.1, 121.0, 120.5, 117.8, 111.8, 52.6, 38.3, 32.0, 29.7, 29.4, 27.2, 26.8, 22.7, 21.2, 14.2; LC–MS (positive mode) *m*/*z*: 498 (M+H)$^+$; Anal. Calcd for $C_{34}H_{47}N_3$ (497.38): C, 82.04; H, 9.52; N, 8.44%. Found: C, 82.00; H, 9.50; N, 8.50%.
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