



Synthesis and photo-physical properties of methoxy-substituted π -conjugated-2,2'-bipyridines

Tanmay Chatterjee, Monima Sarma, Samar K. Das *

School of Chemistry, University of Hyderabad, Hyderabad 500046, AP, India

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ABSTRACT

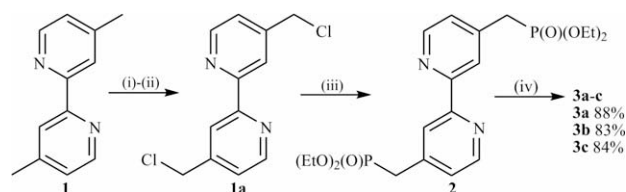
4,4'-Bis-vinyl-2,2' bipyridines have been known in the area of materials chemistry since last few decades. Bipyridine molecules bearing donor substituents in their π backbone are examples of 'push–pull' molecules. Emissive properties of such ligands depend on the position of the donor unit in their π backbone. The Horner–Wordsworth–Emmons reaction has been used extensively to synthesize such types of conjugated systems. Three newly synthesized highly conjugated 2,2' bipyridines (**3a–c**) have been described. The molecules **3a–c** are highly emissive in the visible region at room temperature.

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2,2'-Bipyridines are nitrogen-containing organo-materials with enormous applications in materials chemistry. They readily form complexes with transition metals in which they can interact with the metals via both σ -donating nitrogen atoms and π -accepting M.Os.¹ The resulting complexes are very stable due to the formation of a five-membered chelate. 4,4'- π -conjugated-2,2'-bipyridines have been explored in materials chemistry since last two decades due to their excellent performance in the areas of non-linear optics (NLO),^{2–8} light-emitting diode devices,⁹ electrochemistry,^{10,11} solar cell^{12–14} etc. 2,2'-bipyridines bearing a chromophore or fluorophore in their π backbone constitute a 'push–pull' molecule, where the donor moieties act as the pushing unit and the pyridine moieties are the pulling unit. These systems are synthetically flexible, in which the centrosymmetric or non-centrosymmetric push–pull units are easily accessible via functionalization of 4,4'-dimethyl-2,2'-bipyridine (**1**). The major synthetic strategies in synthesizing such systems include either the classical Knoevenagel Condensation between the deprotonated 4,4'-dimethyl-2,2'-bipyridine and an aromatic aldehyde or Wordsworth–Emmons Reaction between the tetraethyl-2,2'-bipyridine-4,4'-diylbis(methylene)diphosphonate (**2**) and an aldehyde. The resulting highly conjugated molecules are important in the sense that they can be aggregated in a polymeric unit simply by a (transition) metal ion resulting in coordination complexes that have potential to exhibit NLO activity due to intraligand charge transfer (ILCT) or metal–ligand charge transfer (MLCT) transition.⁷ Several homoleptic and heteroleptic complexes exhibiting NLO activity have been reported by Bozec

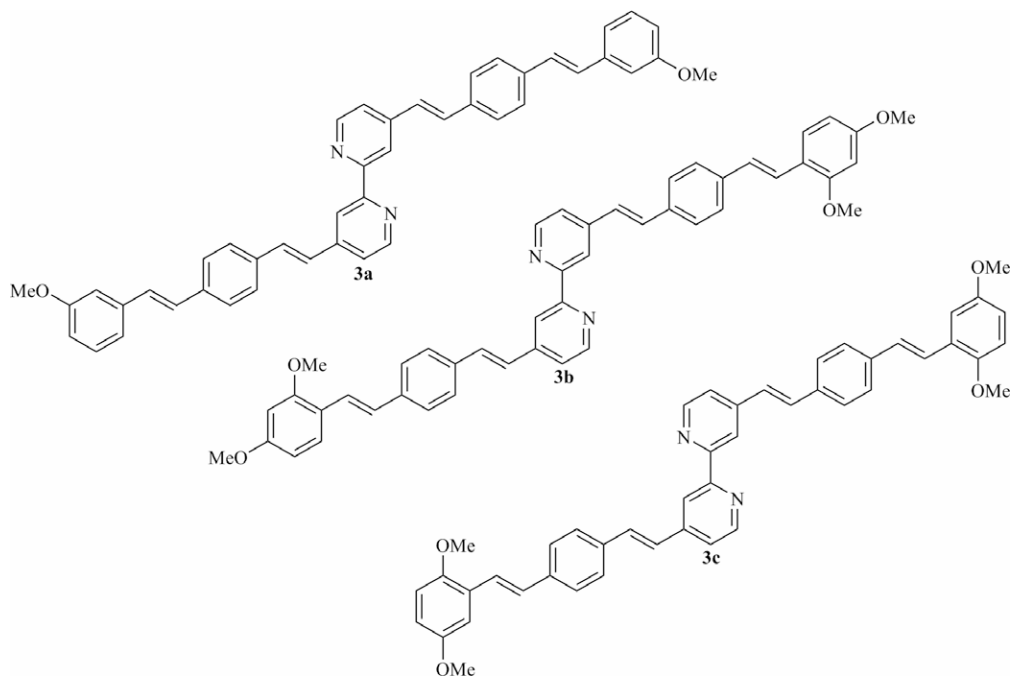
and co-workers.^{2–7} Optical properties of such metal complexes can be easily tuned through variation of substituents at the π backbone of the bipyridine ligands. In this Letter, we have described three newly synthesized highly conjugated 2,2'-bipyridines (**3a–c**) as shown in Schemes 1 and 2. The resulting molecules (that can be used as potential ligands for metal coordination) are highly emissive in the visible region.

Wordsworth–Emmons reaction is a well-known synthetic route for the preparation of 4,4'-bis-vinyl-2,2'-bipyridines with predominantly *E*-selectivity of the C=C vinyl bond as described by the reactions shown in the second part of Scheme 1.¹⁵ The key precursor of the Wordsworth–Emmons reaction is the phosphonate (**2**) which has been prepared by means of an Arbuzov Reaction by treating 4,4'-bis-chloromethyl-2,2'-bipyridine (**1a**) with triethylphosphite (93%). We have synthesized the required starting molecule, 4,4'-bis-chloromethyl-2,2'-bipyridine (**1a**) using an efficient procedure (of preparing 4,4'-bis-halomethyl-2,2'-bipyridines)



Scheme 1. Synthesis scheme for **3a–c** using Wordsworth–Emmons synthetic route. Reagents and conditions: (i) LDA (2.4 equiv), THF, -70 °C, Me_3SiCl (2.2 equiv), 15 s, EtOH (95%); (ii) CsF (4 equiv), C_2Cl_6 (4 equiv), MeCN, 75 °C, 4 h (80%); (iii) $(\text{EtO})_2\text{P}$, 120 °C, 12 h (93%); (iv) $\text{KO}^\text{t}\text{Bu}$, **8a–c**, THF, rt. The structural drawings of **8a–c** are shown in Scheme 3.

* Corresponding author. Tel.: +91 40 2301 1007; fax: +91 40 2301 2460.
E-mail addresses: skdsc@uohyd.ernet.in, samar439@gmail.com (S.K. Das).



Scheme 2. Structural representations of the newly synthesized and highly emissive π -conjugated bipyridines (**3a–c**).

as described by J. Fraser et al.¹⁶ The synthesis involves deprotonation of **1** by lithium diisopropylamide (LDA) followed by trapping of the resulting di-anion with chlorotrimethylsilane (95%) and finally chlorination with a suitable commercially available electrophile, hexachloroethane in the presence of a dry fluoride source (CsF) in acetonitrile (80%) as shown in the first part of Scheme 1. Finally, the Wordsworth–Emmons reaction between **2** and the synthesized methoxy-substituted 4-styryl benzaldehydes (**8a–c**, see Scheme 2 for their structural drawing and preparation) in the presence of KOBu^t in THF at room temperature afforded the desired conjugated 2,2'-bipyridines (**3a–c**) in good yields.¹⁷

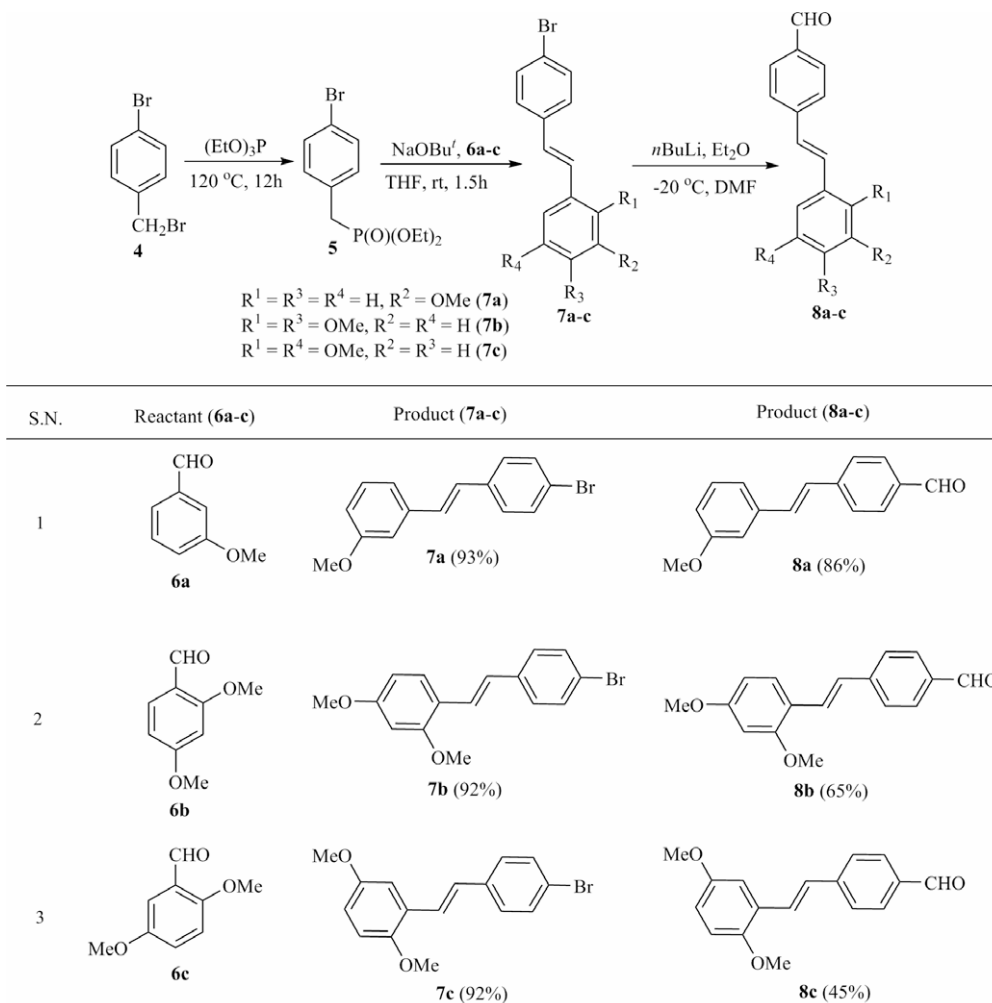
The methoxy-substituted 4-styryl benzaldehydes (**8a–c**) have been synthesized via a three-step procedure starting from 4-bromobenzylbromide (**4**). Treatment of **4** with triethylphosphite results in the corresponding phosphonate derivative (**5**) that undergoes Wordsworth–Emmons reaction with three different methoxy-substituted benzaldehydes (**6a–c**) in THF to produce the corresponding conjugated bromobenzenes (**7a–c**) in good yields.¹⁸ Subsequent lithiation in ether at lower temperature followed by quenching with DMF affords the designed methoxy-substituted 4-styryl benzaldehydes (**8a–c**).¹⁹ Scheme 3 depicts a schematic representation of the syntheses of **8a–c**.

All the synthesized materials have been characterized by NMR spectroscopy including elemental and LC–MS analyses. *E* conformations of the compounds **7a–c** and **8a–c** are clearly understood from the J_{HH} vinylic coupling constant of ca 16 Hz (see Supplementary data for relevant NMR spectra). Molecular structures of the newly synthesized bipyridines (**3a–c**) have been determined by ¹H NMR, LC–MS spectral studies including elemental analyses and the knowledge of the precursors from which they have been synthesized. The major problem associated with the characterizations of this kind of highly conjugated bipyridine materials is their poor solubility in common organic solvents which precludes the detailed solution NMR investigations (for example, ¹³C NMR studies). The low solubility is probably due to the stacking of concerned bipyridine molecules in the solid state.

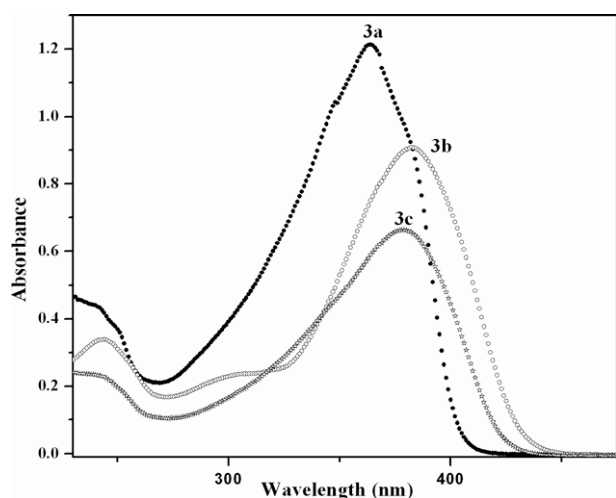
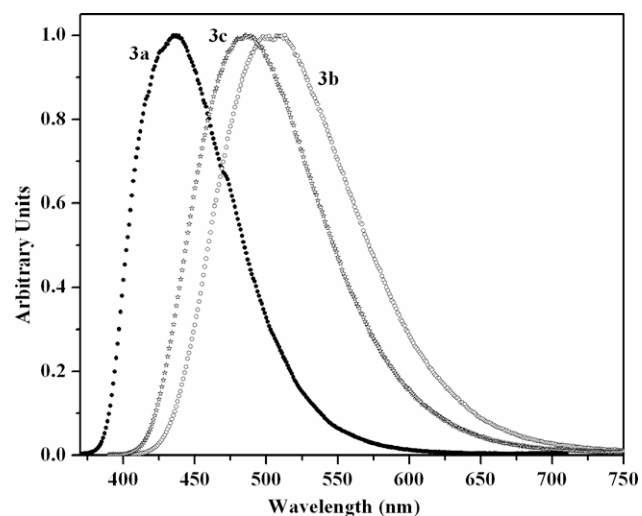
UV–visible and emission spectral studies of **3a–c** have been performed in dichloromethane solution (concentration range: $\sim 10^{-5}$

and 10^{-6} M) at 298 K. The nature of absorption of three compounds **3a–c** is almost identical as shown in Figure 1. Compounds **3a**, **3b** and **3c** show absorption maxima at 365, 384 and 380 nm, respectively (Fig. 1). These absorptions in the UV region are assigned to intra-ligand charge transfer transitions within the molecules.^{2–5} As the molecules bear no chromophores in their π backbones, no absorption band has been observed in the visible region. The room temperature emission spectra of the compounds **3a–c** in dichloromethane revealed band maxima at 435 nm, 505 nm and 488 nm, respectively (Fig. 2, see Table 1), when the excitation wavelengths were 365 nm, 384 and 380 nm, respectively. As a result, at $\lambda_{\text{em}} = 435$ nm (for **3a**), 505 nm (for **3b**) and 488 nm (for **3c**), the excitation spectra exhibit band maxima at 360 nm, 382 nm and 380 nm, respectively. The emission quantum yields (ϕ_{em}) of the compounds **3a–c** at room temperature (using quinine sulfate in 1 N H₂SO₄ as the reference, whose quantum yield is known to be 0.545²⁰) were found to be 0.59, 0.70 and 0.75 respectively.

The molecules were excited at same optical densities where the absorption curve of the sample intersects the same of quinine sulfate (see Supplementary data for relevant spectra). As shown in Figure 2, compounds **3a–c** show excellent emission in 400–600 nm region. The lower homologue of **3c**, namely, 4,4'-di(2-(2,5-dimethoxyphenyl)ethynyl)-2,2'-bipyridine has been reported by Nazeeruddin and Gratzel⁹ that exhibits emission band centred at 450 nm with photoluminescence quantum yield of 0.43 and is one of the highest blue organic light-emitting diode known in literature. It is known that 4,4'-bis-styryl-2,2'-bipyridines become more fluorescent when the two donor groups are in *ortho* and *meta* positions on the phenyl ring.⁹ We have also observed that 4,4'-di(2-(3-methoxyphenyl)ethynyl)-2,2'-bipyridine and 4,4'-di(2-(2,4-dimethoxyphenyl)ethynyl)-2,2'-bipyridine (lower homologues of **3a** and **b**, respectively) have quantum yields of only 0.081 and 0.007; it is amazing that when we increase the conjugation by synthesizing **3a** and **3b**, it enhances the quantum yields drastically ($\phi_{\text{3a}} = 0.59$, $\phi_{\text{3b}} = 0.70$). As expected, **3a–c** show emission maxima that are red shifted compared to the emission maxima of their lower homologues. Spectroscopic data are summarized in Table 1.



Scheme 3. Synthesis of the methoxy-substituted 4-styryl benzaldehydes

Figure 1. UV-visible spectra of **3a-c** in dichloromethane at 298 K.Figure 2. Emission spectra of **3a-c** in dichloromethane at 298 K normalized to 1.

In conclusion, we have succeeded in synthesizing three new π -conjugated 'push-pull' 2,2'-bipyridines. The resulting compounds are highly emissive in the visible range at room temperature. Even though, the title compounds are less soluble in

common organic solvents, they form soluble complexes with the transition metal ions. Further investigation of these highly emissive materials towards light-emitting devices is in progress in our laboratory.

Table 1
Summary of the photo-physical data

Compound	λ_{abs} (nm)	λ_{em} (nm)	ϕ_{em}
3a	365	435	0.59
3b	384	505	0.70
3c	380	488	0.73

Acknowledgements

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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.2010.02.027.

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- Typical procedure for the preparation of the bipyridine (3c)*: Solid potassium *t*-butoxide (4 mmol, 4 equiv) was added at a time to a THF solution (20 ml) of tetraethyl 2,2'-bipyridine-4,4'-diylbis(methylene)diphosphonate (1 mmol) (**2**) and (*E*)-4-(2,5-dimethoxystyryl)benzaldehyde (**8c**) (1.5 mmol, 3 equiv) at room temperature. The resulting yellow turbid reaction mixture was stirred at this temperature until completion (monitored by TLC), which was then quenched with water (1 ml). Subsequently, methanol was added to result in the precipitation of the desired compound (**3c**), which was isolated by filtration, washed with small amount of water, thoroughly with methanol (until the filtrate did not show presence of the aldehyde), ether and dried under vacuum. Orange yellow solid; mp: more than 200 °C; yield = 84%; IR (KBr, cm⁻¹): 3026.58, 2945.57, 2825.97, 1583.70, 1541.26, 1494.97, 1458.32, 1417.81, 1375.37, 1338.72, 1221.05, 1103.38, 1041.65, 954.85, 848.76, 798.60, 709.87, 567.12, 509.25; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.69 (d, *J* = 4.6 Hz, 2H), 8.58 (s, 2H), 7.63–7.65 (m, 12H), 7.42–7.48 (m, 4H), 2.26–2.32 (m, 4H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8 Hz, 2H), 3.81 (s, 6H), 3.76 (s, 6H); we could not record ¹³C NMR because of the less solubility of the compound in common organic solvents; LC-MS (positive mode): *m/z* = 686 (M⁺+H)⁺; elemental Anal. Calcd for C₄₆H₄₀N₂O₄: C, 80.68; H, 5.89; N, 4.09. Found: C, 80.72; H, 5.93; N, 4.12. UV-vis: λ_{max} = 380 nm (in dichloromethane, ~10⁻⁵ M concentration); fluorescence: λ_{em} = 488 nm (in dichloromethane, ~10⁻⁶ M concentration).
- Typical procedure for the preparation of (E)-2-(4-bromostyryl)-2,5-dimethoxybenzene (7c)*: Solid sodium *t*-butoxide (1.92 gm, 20 mmol) was added at a time to a 50 ml THF solution of diethyl 4-bromophenylphosphonate (**5**) (4 gm, 13 mmol) and 2,5-dimethoxybenzaldehyde (**6c**) (10 mmol) at 0 °C. The resulting slurry was warmed up to room temperature and stirred for 90 min. The reaction was quenched with water and extracted with hexane. The combined organic layers were washed with brine solution, dried over Na₂SO₄ and evaporated. The crude product was purified through silica gel column using ethyl acetate/hexane = 5:95 (v/v) as the mobile phase to afford the desired material as white solid in 92% yield. mp: 68–69 °C; ¹H NMR (400 MHz, TMS, CDCl₃): δ 7.38–7.47 (m, 5H), 7.12 (s, 1H), 7.01 (d, 1H, 16 Hz), 6.79–6.85 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H); ¹³C NMR (100 MHz, TMS, CDCl₃): δ 154.54, 152.30, 137.56, 132.50, 131.31, 128.91, 127.60, 124.86, 121.94, 114.80, 113.03, 112.50, 56.99, 56.59; LC-MS (positive mode): *m/z* = 321 (M⁺+2H)⁺; elemental Anal. Calcd for C₁₆H₁₅BrO₂: C, 60.21; H, 4.74. Found: C, 60.28; H, 4.79.
- Typical procedure for the preparation of (E)-4-(2,5-dimethoxystyryl)benzaldehyde (8c)*: *n*-Butyl lithium (2.5 M in hexane) (4 ml, 10 mmol) was added dropwise to a 50 ml ether solution of **7c** (5 mmol) at –20 °C and stirred for 60 min at this temperature, warmed up to 0 °C before DMF (0.77 ml, 10 mmol) was injected. The reaction was continued at this temperature until its completion (TLC) and then it was quenched with water and extracted with ethyl acetate. The combined organic layers were washed once with water then with brine solution, dried (Na₂SO₄) and evaporated. The crude was subjected to column chromatography on silica gel using ethyl acetate/hexane = 20:80 (v/v) to afford the desired material as fluorescent yellow solid; yield: 45%; mp: 52–53 °C; IR (KBr, cm⁻¹): 3045.87, 3005.37, 2951.35, 2831.76, 2739.17, 1819.04, 1695.58, 1599.13, 1493.04, 1425.52, 1284.71, 1244.20, 1211.41, 1120.74, 1047.44, 1020.44, 958.71, 852.61, 792.81, 715.66, 505.40; ¹H NMR (400 MHz, TMS, CDCl₃): δ 9.97 (s, 1H), 7.84 (d, 2H, 8 Hz), 7.58–7.66 (m, 3H), 7.09–7.15 (m, 2H), 6.84 (s, 2H), 3.85 (s, 3H), 3.81 (s, 3H); ¹³C NMR (CDCl₃): δ 191.70, 153.75, 151.81, 143.98, 135.19, 130.21, 127.91, 127.00, 126.93, 126.35, 114.76, 112.30, 111.91, 56.20, 55.83; LC-MS (positive mode): *m/z* = 269 (M⁺+1H); elemental Anal. Calcd for C₁₇H₁₆O₃: C, 76.10; H, 6.01. Found: C, 75.95; H, 6.10.
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