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A Simple Route to Unsymmetric Cyano-substituted Oligo(*p*-phenylene-vinylene)s

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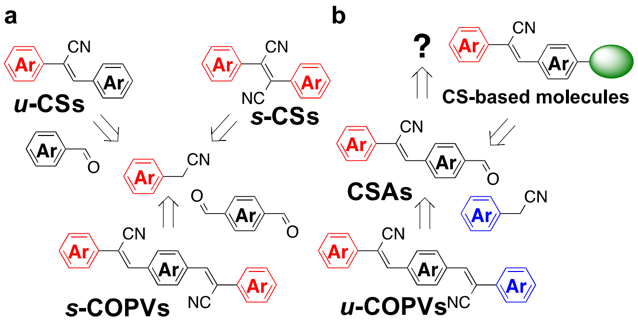
We report here the synthetic route to unsymmetric cyano-substituted oligo(*p*-phenylene-vinylene)s (COPVs), which are not reported so far. These molecules were synthesised in high yield through a simple pathway of step-wise Knoevenagel condensation. The proposed study improves the molecular design strategies of COPVs towards solid fluorescent materials. This synthetic pathway gave various novel COPVs. The properties of the obtained COPVs were also discussed.

π-Conjugated Molecules • Knoevenagel Condensation • Fluorescence • Unsymmetric Structures • Donor-Acceptor

Cyano-substituted stilbenes (CSs) and oligo(*p*-phenylene-vinylne)s (COPVs) have attracted great interest owing to their unique physical properties and applications in organic optoelectronics.[1] These molecules possess unique self-assembly characteristics for nanostructures with enhanced emission and/or efficient carrier transport.[2] Moreover, fluorescent π-conjugated molecules often show aggregation-caused fluorescence quenching; however, cyano-substituted molecules, such as CSs and COPVs, generally exhibit aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE). This is due to the changing of the electric interactions involved into through-bond and through-space interactions.[3] The ristriction of intramolecular rotation (RIR) of the twisted phenylene-vinylene frameworks in the aggregated state offers through-bond and/or through-space interactions. In addition to the efficient solid-state fluorescent behaviour, almost all these molecules possess different and unique fluorescence characteristics. CSs and COPVs have played a crucial role in the recent advances in organic mechanofluorochromic materials.[4] These compounds are synthesised via Knoevenagel condensation of an arylacetonitrile with an arylaldehyde in the presence of a base, usually in high yield. Recent efforts in the molecular design and synthesis of such molecules are focused on the properties that are useful for organic device applications. Since this condensation is an easy synthetic procedure that uses commercially available reagents, various CSs and COPVs have been reported (Scheme 1a). However, so far, the synthesis of some simple CSs and COPVs has been limited.

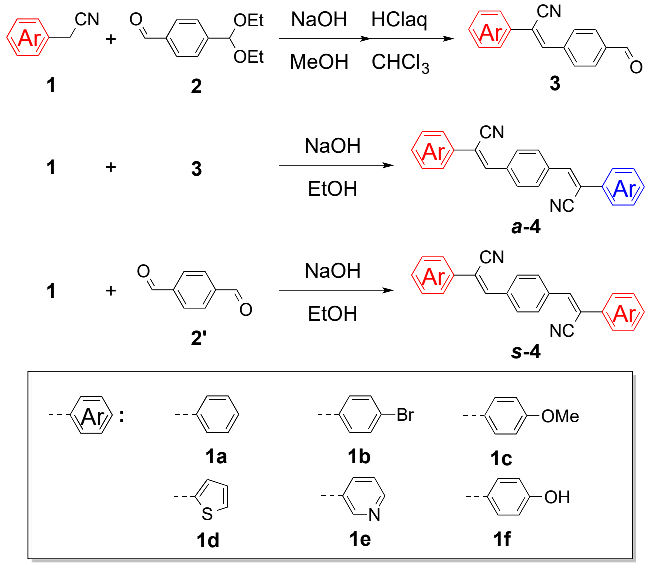
Regioregularity of π-conjugated oligomers and polymers is important for self-assembly and physical properties.[5] An unsymmetric π-conjugated molecule offers the advantages of good solubility, tuneable properties, and assembly.[6] In comparison with the simple symmetric π-conjugated molecules, unsymmetric π-conjugated molecules require selective synthetic strategies. Accordingly, there are several reports on symmetric COPVs, but to the best of our knowledge, few reports on the synthesis of unsymmetric COPVs have been reported.[7] These report on the step-wise synthesis of COPVs, but the synthetic phathway is not efficient[7a] and the purification procedure is not simple[7b]. Oxidative-coupling of arylacetonitriles and the Knoevenagel condensation between arylacetonitriles and arylaldehydes yield both symmetric and unsymmetric CSs (*s*-CSs and *u*-CSs, Scheme 1a).[8,9] Symmetric COPVs (*s*-COPVs) can be easily obtained by the condensation of aryl dialdehydes with arylacetonitriles (Scheme 1a).[10]



Scheme 1. (a) Retrosynthesis of various CSs and symmetric COPVs from previous reports. (b) Retrosynthesis of cyano-substituted stilbene carbardehyde and unsymmetric COPVs from the proposed work.

The combination of the two arene units tunes and controls the physical properties and self-assembly of COPVs. For unsymmetric COPVs (*u*-COPVs), the molecular design is flexible and physical properties can be tuned by choosing the aryl moieties, but there are currently no reports of such a synthetic strategy. CSs with an aldehyde group (CSAs) are key molecules for *u*-COPVs synthesis (Scheme 1b). They are also important building blocks because the aldehyde group is useful not only for the Knoevenagel condensation but also for various synthetic procedures, such as imination, and the Wittig, Aldol and redox reactions.[11] The synthesis of CSAs would allow to obtain various CS-based molecules and *u*-COPVs, which can function as organic emitters and building blocks of oligomeric and polymeric materials (Scheme 1b). In this study, we report the synthesis of CSAs and their Knoevenagel condensation to yield *u*-COPVs.

Scheme 2 displays the synthetic procedure for the novel COPVs. The target compounds can be prepared from a half protected terephthalaldehyde that is employed during the first step of the synthesis. The condensation of a *p*-arylacetonitrile, **1a-d**, with terephthalaldehyde mono(diethylacetal), **2**, was carried out in methanol in the presence of NaOH at room temperature for 10 min. The intermediate, acetal-protected **3**, was easily isolated by filtration because acetal-protected **3** is insoluble in methanol/water (1:1 vol.). Then, the deprotection of the acetal group afforded the CSs with an aldehyde group (CSA), **3a-d**, in good yield (> 89%). The second Knoevenagel condensation, **3a-d** with various arylacetonitriles (**1a-e**) in ethanol in the presence of NaOH, resulted in symmetric (**4aa**, **4bb**, **4cc**, **4dd**) and several unsymmetric (**4ab**, **4ac**, **4ad**, **4ae**, **4bc**, **4bd**, **4be**, **4cd**, **4ce**, **4de**) COPVs in high isolated yield (91%–99%). Also, the condensation of **3a-c** with 4-hydroxyphenylacetonitrile, **1f**, was performed by acid treatment after the reaction, affording monohydroxylated unsymmetric COPVs (**4af**, **4bf**, **4cf**) in good isolated yield (84%–96%). However, the reaction of **3d** with **1f** was not successful, as it resulted in a complicated reaction mixture. Symmetric COPVs (**4aa**, **4bb**, **4cc**, **4dd**, **4ee**, **4ff**) were also synthesised by the condensation of terephthalaldehyde, **2'**, with **1** in high isolated yield. It is worth noting that the purification was very easy (filtering, washing and drying) as COPVs are insoluble in ethanol and methanol.



Scheme 2. Synthesis of CSA, **3**, unsymmetric COPVs, ***a*-4** and symmetric COPVs, ***s*-4**, via Knoevenagel condensation.

UV-vis absorption and fluorescence spectroscopies and quantum yield measurements were performed to investigate the fundamental optical properties of these new compounds (Figures 1, 2, S47-57 and Table 1). All photophysical data are summarised in Table 1.

The UV-vis absorption spectra of **3** in CH_2Cl_2 are presented in Figure 1a. The band energy of **3b** was slightly lower than that of **3a**. Compounds **3c** and **3d**, which have electron-donating 4-methoxyphenyl and 2-thienyl units, respectively, were red-shifted in comparison with **3a** and **3b**. The solid thin-film spectra of **3c** and **3d** also showed red-shifted bands in comparison with **3a** and **3b** (Figure 1b). It is worth noting that **3c** and **3d** showed fluorescence in CH_2Cl_2 (Figure S48), but this was not observed for **3a** and **3b**. This is probably due to the charge transfer (CT) fluorescence based on the donor-acceptor structures.[12] Moreover, these compounds **3** were emitted in the solid state. The quantum yields (Φ) of the solutions and solids were measured based on an absolute method using an integrating sphere equipped with a multichannel spectrometer. The Φ values of **3c** and **3d** in CH_2Cl_2 were 0.26 and 0.25, respectively. The solid state Φ values were higher than those in CH_2Cl_2 (Table 1). The methoxy group effectively increased the quantum yield.

Table 1. Photophysical data of compounds

	In CH_2Cl_2			Solid[b]		
	λ_{abs} (nm)	λ_{fl} (nm)	Φ[a]	λ_{abs} (nm)	λ_{fl} (nm)	Φ[a]
3a	331	-	-[c]	333	496	5
3b	333	-	-[c]	342	497	23
3c	354	485	26	367	540	56
3d	363	448	25	396	517	33
4aa	347	-	-[c]	-[e]	517	96
4ab	372	-	-[c]	-[e]	544	45
4ac	381	500	38	-[e]	500	99
4ad	380	-	-	-[e]	547	38
4ae	363	-	-[c]	-[e]	548	50
4af	373	496	21	-[e]	550	< 1
4bb	373	-	-[c]	-[e]	523	9
4bc	383	492	29	-[e]	558	82
4bd	404	496	28	-[e]	619	36
4be	370	-	-[c]	-[e]	547	20
4bf	377	497	70	-[e]	528	< 1
4cc	377	491	36	-[e]	547	97
4cd	400	502	66	-[e]	559	12
4ce	382	521	57	-[e]	583	98
4cf	376	492	65	-[e]	533	< 1
4dd	392	492	10	-[e]	592	15
4de	382	500	24	-[e]	594	28
4ee	360	-	-[c]	-[e]	534	50
4ff	392[d]	489[d]	84[d]	-[e]	-	-

[a] Absolute fluorescence quantum yields determined with a calibrated integrating sphere system (average Φ value measured 5 times, errors < 3%).[b] Cast courted on glass plate.[c] <0.1 or = 0.[d] In DMSO.[e] The spectrum was not clearly obtained.

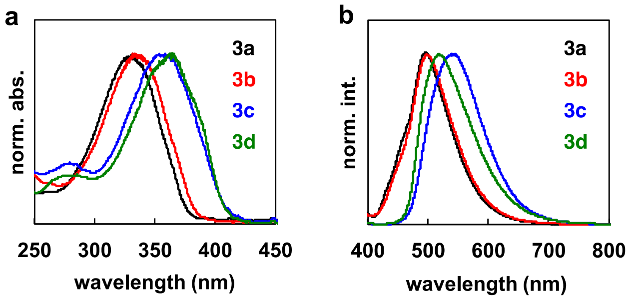


Figure 1. (a) UV-vis absorption in CH_2Cl_2 and (b) solid-state fluorescence spectra of **3**.

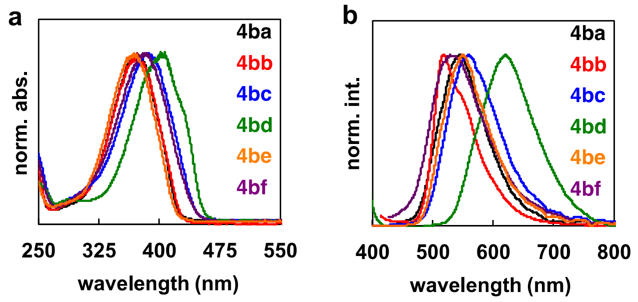


Figure 2. (a) UV-vis absorption in CH_2Cl_2 and (b) solid-state fluorescence spectra of **4bx**.

We focused on the absorption spectra of **4bx** in CH_2Cl_2 and solid-state fluorescence spectra of **4bx** to analyse the properties and differences in symmetric and unsymmetric COPVs (Figure 2). The spectra of **4bx** showed lower energy bands than **3b** due to the extension of the π-conjugated system (Figure 2b). The peaks of **4bx** were located between 372–401 nm. The spectra of *u*-COPVs (**4ba** and **4be**), which have phenyl and 3-pyridyl groups, showed peaks at *ca*. 372 nm. These were similar to that of *s*-COPVs (**4bb**). Furthermore, *u*-COPVs with electron-donor units (**c**, **d**, **f**) showed slightly red-shifted bands due to the intramolecular CT interaction[12] between the electron-donating units and the electron-acceptor cyano-substituted vinylene.

Compounds **4bx** showed fluorescence in the solid state (Figure 2b). In addition, **4bc**, **4bd** and **4bf** showed fluorescence in solution (CH_2Cl_2). Introduction of the electron-donor units into the molecules resulted in fluorescence in both solution (isolated state) and solid (aggregated state). The solid-state spectra of **4bx** (518–631 nm) exhibited lower energy fluorescence bands than those in CH_2Cl_2 (Figure S50) owing to the intramolecular CT interaction in solids. The spectra of *u*-COPVs exhibited lower energy than that of *u*-COPV (**4bb**) due to CT fluorescence. Moreover, the compounds with a *p*-methoxyphenyl unit had relatively high Φ value in solid. A strong electron-donor unit, thienyl, dramatically decreases the energy band due to an effective CT interaction. The compound with a *p*-hydroxyphenyl unit (**4bf**) showed higher Φ in CH_2Cl_2 than in solid state, although the other compounds showed AIE or AIEE [13]. Therefore, incorporation of a hydroxyl group results in an opposite trend.

In summary, we synthesised cyano-substituted stilbenes with an aldehyde group, **3**. Their Knoevenagel condensation with different arylacetonitriles afforded symmetric and unsymmetric cyano-substituted oligo(*p*-phenylene-vinylne)s, **4**. π-conjugated compounds were successfully synthesised. The absorption and fluorescence properties of the molecules can be tuned based on the synthetic strategy. Further studies based on the synthesis of various unsymmetric cyano-substituted oligo(*p*-phenylene vinylne)s and reactions of **3** with various reagents are currently in progress. Moreover, the possible applications of COPVs (such as flexible crystal engineering of π-conjugated molecules[14] and chromism[15,16]) are also under investigation.

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