Cyanurate-guided self-assembly of a melamine-capped oligo(*p*-phenylenevinylene)†

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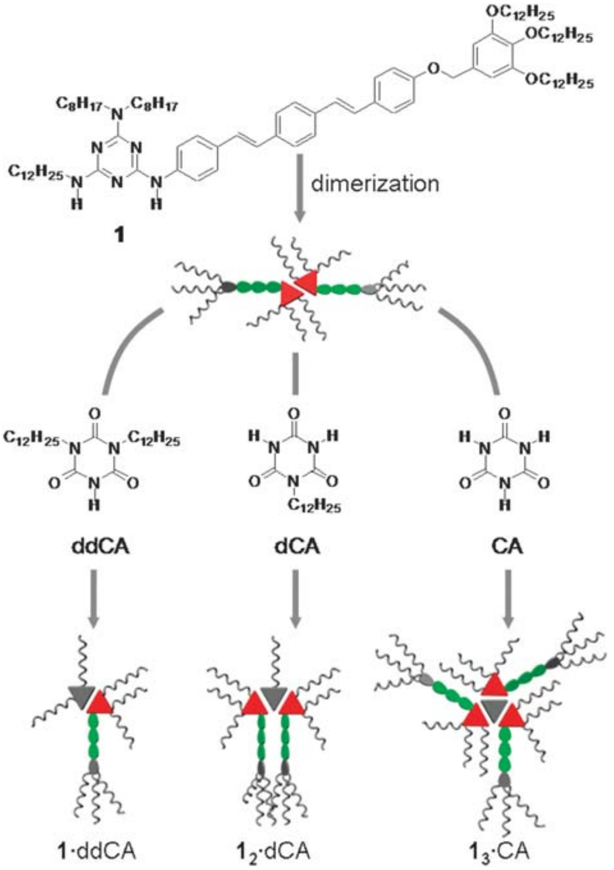
An oligo(*p*-phenylenevinylene) capped on one end by a monotopic DAD-type triple hydrogen-bonding module shows distinct optical properties as well as self-organization behavior upon complexation with cyanurates with different numbers of ADA-type triple hydrogen-bonding sites.

Multiple hydrogen-bonding interactions between heterocyclic compounds have been widely used to regulate the spatial arrangements of functional dye molecules on the molecular scale.[1,2] Recent interests are being directed toward the construction of higher-order complex superstructures hierarchically organized from hydrogen-bonded dye assemblies.[2–6] Owing to their directionality, multiple hydrogen-bonding interactions are very reasonable noncovalent glues for the bottom-up creation of functional materials composed of highly-organized optoelectronically active components because of the predictable shapes of hydrogen-bonded species. Such optoelectronically active superstructures with highly-restricted dimensionalities of the molecular array are expected to offer unique properties as organic devices. The research progress in this direction has been led by Schenning, Meijer *et al.*, who succeeded to give not only attractive nanostructures but also deeper insights into self-assembling principles,[3f] supramolecular chirality,[3g,h] and energy/electron transfer,[3c,e] by using hydrogen-bonding oligo(*p*-phenylenevinylene)s (OPVs).

Recent efforts in our group have been devoted to the construction of dye assemblies based on well-established melamine–barbiturate/cyanurate hydrogen-bonding systems,[6] where the shapes of supramolecular species can be diversified by changing the structures of non-dye components and binding stoichiometries. This approach enables the creation of diverse superstructures of functional dyes with distinct optical properties. By using OPV as a functional chromophore segment, here we report a new method to diversify the self-organization process and optical properties of functional components based on the complexation between melamines and cyanurates.[7]

Melamine-linked OPV **1** was synthesized as a π-electronic supramolecular building block and characterized by ^{1}H NMR, FAB-MS and elemental analysis (see ESI†). As complementary hydrogen-bonding components, we used ddCA, dCA and CA, which are monotopic, ditopic and tritopic triple hydrogen-bonding modules, respectively. Thus the complexation of **1** with these cyanurates should produce supramolecular species with different numbers of OPV segments (Scheme 1), which are expected to undergo distinct hierarchical organization.

A diluted methylcyclohexane (MCH) solution of **1** (c = 1 × 10^{-5} M) shows an absorption maximum (λ_{max}) at 376 nm



Scheme 1 Schematic representation of complexation of **1** with cyanurates.

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization data of **1**. Fluorescence spectrum of monomeric **1**. UV/Vis titration of **1** with ddCA. SEM images of **1**$_2$·dCA. See DOI: 10.1039/b808684b

Table 1 Absorption maxima (λ_{max}/nm) of **1** and its stoichiometric mixtures with cyanurates in MCH at 10 °C. Spectra at 5×10^{-4} M are shown in Fig. 1a

[**1**]/mol L^{-1}	1×10^{-5}	1×10^{-4}	5×10^{-4}
1	376	371	365
1·ddCA	376	376	378
$\mathbf{1}_2$·dCA	357	355	355
$\mathbf{1}_3$·CA	376	376	363

identical to that observed in chloroform, indicating that **1** is in a molecularly-dissolved state in MCH at this concentration. Upon increasing the concentration, λ_{max} was gradually blue-shifted and subsided to 365 nm at 5×10^{-4} M (Table 1 and black line in Fig. 1a). This result suggests that π-stacked aggregation of **1** takes place upon increasing the concentration, probably *via* the dimerization through the double hydrogen-bonding interaction between melamine moieties (Scheme 1).

When 1 equivalent of monotopic ddCA was added to the solution of **1** at a concentration of 1×10^{-5} M where no π-stacking takes place, λ_{max} hardly shifted. Above 1×10^{-4} M where the self-aggregation of **1** takes place, however, λ_{max} moved to the position of the free OPV in the presence of ddCA (Table 1 and red line in Fig. 1a), demonstrating that the π-stacked aggregation of dimerized **1** indeed takes place which is disrupted by the formation of complex **1**·ddCA having a lesser π-conjugated plane (Scheme 1). UV/Vis titration experiments at a concentration of 5×10^{-4} M displayed 1 : 1 complexation by the quantitative formation of DAD ADA hydrogen-bonding pair (see ESI†).

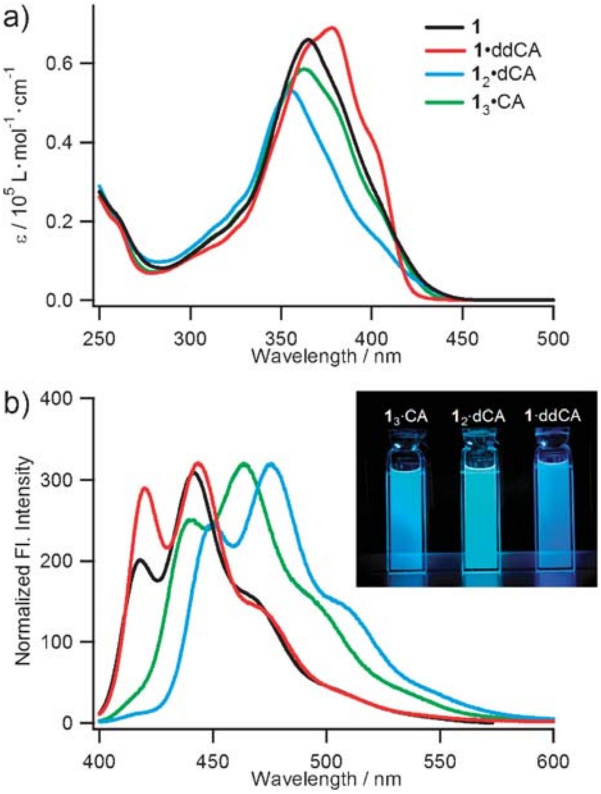

Fig. 1 (a) UV/Vis and (b) normalized fluorescence spectra of MCH solutions containing stoichiometric mixtures of **1** (c = 5×10^{-3} M) and cyanurates at 10 °C. Black, **1** (λ_{max} = 365 nm); red, **1** + ddCA (λ_{max} = 378 nm); blue, **1** + dCA (λ_{max} = 355 nm); green, **1** + CA (λ_{max} = 363 nm). Fluorescence spectra were measured by front-face illumination setup.

In sharp contrast, the addition of 1/2 equiv. of ditopic dCA gave rise to a blue shift of λ_{max} up to 357 nm, even at a concentration of 1×10^{-5} M (Table 1). Because of this relatively large blue shift (blue line in Fig. 1a), a UV/Vis titration experiment for 1×10^{-5} M showed a gradual blue shift (376 → 357) upon addition of dCA up to 0.5 equiv., confirming the quantitative formation of a 2 : 1 complex. Interestingly, λ_{max} of the resulting complex $\mathbf{1}_2$·dCA does not change significantly across a wide concentration range from 1×10^{-6} M to 5×10^{-4} M (Table 1). It is likely that the π-stacking interaction occurring for this complex is different from that of dimerized **1** leading to one-dimensional stacks, in view of the stability (no concentration-dependence) and stacking arrangement (larger blue shift). By invoking our recent study on hydrogen-bonding perylene bisimides,[6f] the formation of a π-stacked dimer of **1** locked by dCA through triple hydrogen-bonding interactions is strongly suggested (Scheme 1).

In the case of 1/3 equiv. of tritopic CA, we again saw only a marginal change of λ_{max} of **1** at concentrations of 1×10^{-5} and 1×10^{-4} M (Table 1). This finding has a significant meaning because it shows the absence of "intra-supramolecularly" π-stacked OPV moieties as observed for $\mathbf{1}_2$·dCA in the complex $\mathbf{1}_3$·CA. At a concentration of 5×10^{-4} M, λ_{max} shifted to 363 nm which does not change upon a further increase in concentration (green line in Fig. 1a). Thus, a propeller-type supramolecular structure as shown in Scheme 1 is proposed for complex $\mathbf{1}_3$·CA, which can hierarchically organize into extended columnar-type assemblies.

One of the striking features of the present system is that distinct fluorescence emanated from complexes $\mathbf{1}_n$·cyanurate as a consequence of different aggregated states of OPV chromophores (Fig. 1b). A MCH solution of **1** with a concentration of 5×10^{-4} M shows a structured fluorescence spectrum with maxima ($\lambda_{em\text{-}max}$) at 418 and 442 nm, the positions of which are characteristic of monomeric OPV chromophores (black line).[8] However, the intensity of the longer-wavelength emission band relative to the shorter-wavelength one is higher compared to the spectrum of monomeric **1** measured at a concentration of 1×10^{-5} M,† illustrating the presence of emission from aggregated species at the longer wavelength region. Thus, **1**·ddCA, free from π-stacking interactions even at a concentration of 5×10^{-4} M, exhibited a completely monomeric spectrum ($\lambda_{em\text{-}max}$ = 443 and 420 nm, red line). In sharp contrast, $\mathbf{1}_2$·dCA showed $\lambda_{em\text{-}max}$ at a greatly red-shifted position ($\lambda_{em\text{-}max}$ = 476 and 450 nm, blue line), reflecting a strong H-type electronic interaction of OPV chromophores within the dimeric structure. Emission from self-assembled $\mathbf{1}_3$·CA showed a moderate red-shift ($\lambda_{em\text{-}max}$ = 463 and 440 nm, green line). The π-stacking interaction of this complex is thus weaker than that of $\mathbf{1}_2$·dCA but stronger than that of (dimeric) **1**. Such a difference in the emission wavelength is discernible by the naked eye (inset in Fig. 1b).[9]

When complex solutions were prepared in MCH with a relatively high concentration (5×10^{-3} M) by cooling homogeneous hot solutions to 15 °C, the difference in their hierarchical organization behavior become apparent (Fig. 2a and b).

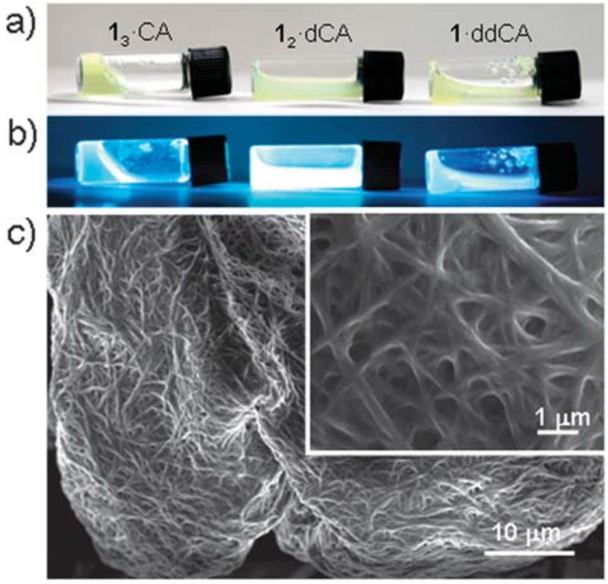

Fig. 2 Photographs of stoichiometric mixtures of **1** ($c = 5 \times 10^{-3}$ M) and cyanurates in MCH at 15 °C taken after cooling from homogeneous hot solutions (a) under room light and (b) under a 365 nm UV-lamp. (C) SEM images of precipitates formed in the solution of complex **1**·ddCA.

Complex **1**·ddCA precipitated upon cooling. Interestingly, SEM observations revealed that the precipitates are heavily-entangled fibres of several hundreds of nanometres in width. This result demonstrates the propensity of this complex to organize into quasi-one-dimensional nanostructures. Complex $\mathbf{1}_2$·dCA is, on the other hand, a suspension below 15 °C and soluble at 20 °C. The high solubility of this complex nicely illustrates the occurrence of π-stacking interactions only within the complex ("closed" π-stacking). No well-defined nanostructures could be visualized for this complex by SEM after evaporating the solvent.† Impressively, $\mathbf{1}_3$·CA produced a transparent organogel.[9,10] Although we have not yet succeeded to visualize the nanostructures formed from this complex by using SEM, this finding indicates the formation of fibrous nanostructures as a result of extended columnar organization of $\mathbf{1}_3$·CA (Scheme 1). Visualization of the nanostructure constructed from this complex by using high-resolution AFM is underway.

In conclusion, we have demonstrated that by mixing a OPV capped at one end by a monotopic triple hydrogen-bonding site (melamine) with complementary mono-to-tritopic triple hydrogen-bonding modules (cyanurates), its optical properties and self-organization behavior are diversified through the complexation with different stoichiometries. The crucial role of the triple hydrogen-bonding interaction here is the construction of hydrogen-bonded supramolecular species with distinct shapes, which determines their association behavior. This strategy can be applied to other functional chromophores to diversify their material morphologies, and optical and electronic properties.

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