The formation of hetero-dimers of bifunctional oligo(p-phenylenevinylene) and C₆₀ ureido-pyrimidinone derivatives has been observed by ¹H-NMR and fluorescence techniques.

Recently, supramolecular architectures have received considerable attention, especially in the field of polymer-based electronics. A great variety of fundamental studies have been carried out concerning electron and energy transfer in non-covalently bonded donor–acceptor systems. Frequently, two or threefold hydrogen bonding arrays are used as selective coupling units between the chromophores. However, a consistently reappearing difficulty in these studies is the low strength of these components, resulting in poor binding characteristics of the studied compounds.

Quadruple hydrogen bonding arrays like the 2-ureido-4[H]-pyrimidinone (UP) unit are excellent building blocks to enhance these interactions and obtain well-defined supramolecular polymers and cycles. The UP unit consists of a self-complementary quadruple hydrogen bonding array with a dimerisation constant of $6 \times 10^3$ M⁻² in chloroform and $6 \times 10^4$ M⁻¹ in toluene. Previous studies concerning this hydrogen bonding unit have shown the formation of very stable structures and the possibility to tune the equilibrium between polymers and cycles. In general, mixing of different species always leads to a statistical mixture of homo- and hetero-dimers due to the self-complementary nature of the system, although in few cases specific dimerisation is observed.

In this work, we report the first observation of preferential formation of functional supramolecular hetero-dimers linked by a self-complementary quadruple hydrogen bonding unit. The obtained hetero-dimer consists of an oligo(p-phenylenevinylene) (OPV) and fullerene (C₆₀) UP derivative (Fig. 1). The OPV derivative (OPV₂-UP₂) consists of two OPV-ureido-pyrimidinone units linked by a C₁₂ spacer at the 6-position of the isocytosine rings. The fullerene derivative (C₆₀-UP₂) has a single C₆₀ molecule attached to two ureido-pyrimidinone units.

A ¹H-NMR spectrum of an equimolar mixture of OPV₂-UP₂ and C₆₀-UP₂ in CDCl₃ displays five peaks at low field (Fig. 1) that are ascribed to the OPV₂-UP₂/C₆₀-UP₂ hetero-dimer (Fig. 2). These peaks are observed at chemical shifts significantly differing in position as compared to the spectra of the separate OPV₂-UP₂ ($\delta = 13.1, 12.1$ and $10.9$) and C₆₀-UP₂ ($\delta = 12.9, 11.6$ and $10.7$) homo-polymers. Therefore it can be concluded that the 1:1 mixture of the two compounds results in the selective formation of cyclic hetero-dimers and not a statistical mixture. The alternating OPV₂-UP₂/C₆₀-UP₂ polymer (which results in an identical ¹H-NMR spectrum) is not assumed to be present as the viscosity of the solution is similar to that of pure chloroform. In addition, the concentration is too low to create polymeric structures.

To investigate the properties of this unique aggregate in more detail, the intensity of the OPV₂-UP₂ fluorescence at $\lambda_{em} = 494$ nm was monitored upon addition of C₆₀-UP₂ in chloroform and toluene. During the addition the positions of the absorption bands remain unchanged, indicating a weak electronic inter-
action in the ground state. However, this addition leads to a distinct quenching of the donor fluorescence, indicating the presence of singlet-energy transfer from the photoexcited OPV to the C$_{60}$ moiety. Electron transfer does not occur to significant extent between OPV and C$_{60}$ under these conditions because of an unfavourable energy for charge separation and the relatively long distance between the chromophores. The quenching rate in a 1:1 (equimolar mixture of molecules) and a 1:2 (equimolar mixture of chromophores) OPV$_2$UP$_2$/C$_{60}$UP$_2$ solution is monitored in time as the high stability of the species present, prevents an instantaneous equilibrium formation (Fig. 3).

The mathematical fit of the experimental data with a double exponential decay results in time constants of 15 and 14 min in the case of respectively the 1:1 and 1:2 mixture in chloroform, whereas in toluene time constants of 180 and 86 minutes are calculated for the 1:1 and 1:2 mixture respectively. These time constants give an indication of the time to reach equilibrium, whereas in toluene time constants of 180 and 86 minutes are the case of respectively the 1:1 and 1:2 mixture in chloroform, together with the exponential decay curves. The high stability of the species present, indicates that the homo-polymeric species are highly stable in chloroform and toluene, whereas in chloroform to toluene, an increase in magnitude increase of the dimerisation constant of the UP unit. This is in full agreement with the doubling of the time constant in toluene when only half the concentration of OPV$_2$UP$_2$ is added, resulting in an immediate quenching of the OPV fluorescence. The examined mixtures were then cooled. Reheating the solution resulted in similar intensities as obtained in the cooling run, demonstrating the reversibility of the interactions. The fluorescence intensities at 20 °C are the same as obtained by addition of the C$_{60}$ derivative at 20 °C. This indicates that the addition of C$_{60}$UP$_2$ at various temperatures does not influence the final state of the mixture. Furthermore, heating of a 1:1 mixture, which had been kept at room temperature equilibrium for one day, resulted in the same fluorescence intensities as in the case of adding C$_{60}$UP$_2$ at 80 °C. A change in fluorescence results only from the breaking of a OPV$_2$UP$_2$/OPV$_2$UP$_2$ couple followed by the formation of a OPV$_2$UP$_2$/C$_{60}$UP$_2$ couple. Therefore, the calculated equilibrium time constant holds the sum of various processes i.e. the opening and closing of the hydrogen bond and the chance of two different non-bonded units colliding. This is in full agreement with the doubling of the time constant in toluene when only half the amount of the C$_{60}$-UP$_2$ is present. The time constants indicate that the homo-polymeric species are highly stable in toluene because the exchange between different species proceeds very slow. The increase in time constants going from chloroform to toluene, can be rationalized by the one order of magnitude increase of the dimerisation constant of the UP unit.

Fig. 3 Fluorescence intensity of 1:1 and 1:2 OPV$_2$UP$_2$/C$_{60}$-UP$_2$ mixtures in chloroform and toluene together with the exponential decay curves. I$_{0}$ represents the fluorescence intensity of the pure OPV$_2$UP$_2$ solution, whereas I$'$ indicates the OPV$_2$-UP$_2$ fluorescence in the indicated mixture. The concentration of OPV$_2$UP$_2$ is 5 × 10$^{-7}$ M, $\lambda_{ex} = $ 435 nm, $\lambda_{em} = $ 494 nm, T = 20 °C.

This accounts for an increased thermodynamic penalty for the presence of non-bonded hydrogen bonding moieties, inducing a considerably lower concentration of free end groups that have the possibility to form new hetero-dimers. Therefore the time needed to reach equilibrium rises in toluene and can be adjusted by increasing the driving force to form equilibrium by enhancing the concentration of one of the compounds. Important is the fact that even though the dynamics of the equilibrium change with solvent, this does not influence the final composition of the mixture. Moreover, the amount of quenching (l$'$/I$'$ > 2 at ratio 1:1) reveals that the formation of OPV$_2$UP$_2$/C$_{60}$-UP$_2$ hetero-couples is favourable as compared to the formation of the respective homo-couples, consistent with the $^{1}$H-NMR results.

Although the l$/I'$ value obtained by fluorescence studies for the ratio of 1:1 of OPV$_2$UP$_2$/C$_{60}$-UP$_2$ is larger than the estimated value of 2, the selectivity for the formation of hetero-dimers is less than was indicated by $^{1}$H-NMR measurements. In the case of an exclusive presence of hetero-dimers, fluorescence quenching is expected to be faster for the equimolar ratio of OPV$_2$UP$_2$/C$_{60}$-UP$_2$, however the addition of an extra amount of C$_{60}$-UP$_2$ (e.g. a 1:2 ratio) leads here to an increase of the fluorescence quenching as the l$/I'$ value increases from 3 to 6. This difference between the fluorescence and $^{1}$H-NMR results is likely to be caused by the large difference in experimental concentration between both techniques.

In conclusion, for the first time the preferential formation of dimeric OPV$_2$UP$_2$/C$_{60}$-UP$_2$ hetero-cyclic structures based on the self-complementary UP quadruple hydrogen bonding unit has been inferred from $^{1}$H-NMR studies in chloroform. Fluorescence studies confirm the occurrence of preferential formation of hetero-dimers, although the selectivity is less at lower concentrations (10$^{-6}$ M). The time for the equilibrium to settle is on the scale of minutes and temperature or solvent type has no effect on the final equilibrium state of the mixture. However, an increase in dimerisation constant by varying the solvent, leads to an enhancement of the stability of the formed species.

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Notes and references