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Quantitative Supramolecular Hetero-dimerization for Efficient Energy Transfer

Guanglu Wu, Zehuan Huang, Oren A. Scherman *

Abstract: The challenge of quantitatively forming selfassembled hetero-dimers without other equilibrium byproducts is overcome through self-sorting favored by the introduction of designed shape-complementary moieties. Such a supramolecular strategy based on CB[8]-directed dimerization is further applied to generate hetero-chromophore dimers quantitatively, leading to efficient energy transfer (> 85 %) upon photoexcitation.

Molecular design for the precise arrangement of lightabsorbing chromophores is critical to realize the next generation of synthetic assemblies for (photo)energy applications. In the light-harvesting systems of photosynthesis, chromophores like chlorophylls and carotenoids are immobilized inside rigid protein scaffolds with specific alignments so as to competently capture photons and transmit the resultant excitation energy to the reaction centre.^[1,2] Thus it can be seen that an efficient energy transfer requires a) an appropriate arrangement of chromophores with specific orientation, stacking, and spacing in order to ensure an effective interchromophoric interaction;^[3] and b) a rigid scaffold to accommodate them so as to sustain the effective arrangement and interaction for a sufficiently long period of time.

Synthetic rigid scaffolds capable of facilitating interchromophoric coupling can be realized by connecting finite number of chromophores with appropriate spacer moieties either through covalent linkage^[4–6] or interlocked mechanical bonding.^[7-9] This often results in discrete entities such as foldamers^[4,10] or cyclophanes^[11–13] in solution, within which the relative arrangement of chromophores can be adjusted by the spacer, [4,14,15] the solvent, [16,17] or external stimuli.^[7,18] Although chromophore assemblies can also be fabricated through non-covalent interactions, they usually lead to uncontrolled aggregation in solution.^[19,20] Macrocyclic hosts such as cucurbit[n]uril (CB[n], n = 6-8, $10)^{[21-23]}$ are utilized to avoid arbitrary aggregates by encapsulating chromophores inside the cavity.^[24-30] In particular, the cavity of CB[8] is able to accommodate chromophore dimers (typically referred to as homo- and heteroternary complexes),^[31,32] although the resultant complexes are often

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Angew Chem Int Ed

too dynamic to sustain long-lived interchromophoric coupling.

Recently, we have demonstrated a non-covalent strategy to stack two chromophores based on bis(N-arylpyridinium) (BAP) derivatives through multiple CB[8] clamping,^[33–36] which has been applied to fabricate supramolecular complexes with emerging features such as red-shifted ab-sorption,^[33,35] enhanced emission,^[35,37-39] directional selfsorting,^[40,41] and a negative pKa shift.^[42] More importantly, the resultant chromophore dimers typically exist as single entities for > 30 ms. The pseudo-static nature of these dimers in aqueous solution provides an excellent scaffold to facilitate long-lived interchromophoric coupling.^[36] This supramolecular approach is particularly convenient to readily produce hetero-dimers through simple mixing unlike covalent linkages^[17] or mechanical interlocking^[8,9] currently required to prepare similar hetero-dimers through rigorous synthesis and purification. The critical challenge for this non-covalent strategy, however, is to generate a

Figure 1 a) Statistical dimerization with the coexistence of three species (AA, BB, and AB). b) Quantitative supramolecular heterodimerization is realized through well-designed shape complementarity between end-groups, which can be further applied to generate c) pure hetero-chromophore dimers with efficient energy transfer. The Cl^- counterions are omitted for clarity.



Figure 2¹H NMR spectra of CB[8]-directed homodimers of a) **VOMe**, c) **VNH**₂, d) **VNMe**₂, f) **VH**, and the equilibrium products of b) a 50/50 mixture of **VOMe** and **VNH**₂ homodimers as well as e) a 50/50 mixture of **VNMe**₂ and **VH** homodimers. g) The equilibrium constant *K* obtained from integration analysis displays a correlation with the shape complementarity between end-groups. h) ROESY NMR spectrum of **VNMe**₂ and **VH** homodimer mixture shows a clear cross-correlation between the *N*,*N*-dimethylamino substituent of **VNMe**₂ and the phenyl group of **VH**. The Cl⁻ counterions are omitted for clarity.

hetero-dimer in a "quantitative" manner,^[43,44] *i.e.* without homo-dimers as equilibrium by-products. In particular, amongst the reported cucurbituril-based self-sorting systems, the majority of them have focused on controlling orthogonal binding modes or sequence specificity;^[45–50] however, few have attempted to harvest hetero-dimers in equilibrated systems^[41,51] and none have succeeded in doing this quantitatively.

Simply mixing two homo-dimers (AA and BB) readily generates hetero-dimer (AB) but not quantitatively, resulting in equilibrium products with a coexistence of all three species (AA, BB, and AB; Fig. 1a).^[41,52-54] Two BAP derivatives, VOMe and VNH₂, have been shown to form 2:2 complexes with CB[8] resulting in homo-dimers with similar binding free energies.^[33] As demonstrated by ¹H-NMR in Fig. 2b, an equimolar mixture of these two complexes instantaneously produce a statistical distribution of three species in solution, which includes the two original homo-dimers (with signals identical to those in Fig. 2a,c) and a third species corresponding to the hetero-dimer complex. An additional set of peaks emerges for the each proton of VOMe, VNH2 as well as CB[8], corresponding to the newly formed hetero-dimer. Integration analysis (e.g. methyl protons at 3.6 ppm) displays a discrete binomial distribution for the three species with a [AA]:[AB]:[BB] ratio of 1:2:1, suggesting that **VOMe** and **VNH**₂ are randomly associated with each other to form dimers with CB[8]. The equilibrium constant K (Eq. 1; Fig. 2g)^[41] for this statistical exchange is calculated to be 1.

$$K = \frac{([AB]/2)^2}{[AA][BB]}$$
(1)

One would expect an extremely large value of K (ideally infinity) upon quantitative hetero-dimer formation. This requires highly selective self-sorting between A and B with suppression of self-recognition (AA and BB)^[55] and a substantial elevation of self-discrimination (AB)^[56] at equilibrium. Würthner et al. suggested that appropriately designed shape complementarity combined with short-ranged attractions may provide an effective route to hetero-aggregates through self-sorting.^[57,58] We have recently shown that the homo-dimer stacking of BAP derivatives with CB[8] is susceptible to the bulkiness of substituents at both ends of the complex.^[34,36] Large substituents lead to stacking with a large slippage between chromophores along the longmolecule axis on account of steric clash.^[34] We therefore posited that a quantitative hetero-dimer AB could be realized through a careful selection of a large end-group for A and a complementary small end-group for B. Thus in a



Figure 3 ¹H NMR spectra of a) **Np14CMe₂**, c) **Ant910H**, and b) their equimolar mixture with two equivalents of CB[8], which displays a proximal stacking between the isopropyl moiety of **Np14CMe₂** and the phenyl group of **Ant910H** demonstrated by d) 2D NOESY NMR at 278 K. All protons are unambigiously assigned through 2D COSY and NOESY NMR (Fig. S16-S17). e) Complex ion peaks with four charges (z=4) and a m/z centered around 916 in the ESI-MS confirm the formation of **[Np14CMe₂•Ant910H•CB[8]**₂]⁴⁺ hetero-dimer. The Cl⁻ counterions are omitted for clarity.

50/50 mixture of A and B, the self-recognition product AA is not favored on account of designed steric crowding, while the preferred self-discrimination product AB will be significantly enhanced by shape-complementarity of the big and small end-groups (Fig. 1b).

Replacing the methoxy group in VOMe with a N,Ndimethylamino (NMe₂) substituent yields another BAP derivative VNMe₂ bearing a bulkier end-group. A 50/50 mixture of the homo-dimers VNMe₂ and VNH₂ displays an equilibrium mixture significantly dominated by the heterodimer (92 %) along with trace amounts of homo-dimers, as shown in Fig. S2, resulting in a K value of 129. In addition to increasing the size of one of the end-groups (*i.e.* VNMe₂), a reduction to the size of the complementary end-group (from VNH₂ to VH) (Fig. 2g) should further increase the value of K. Fig. 2e displays an equimolar mixture of VNMe2 and VH homo-dimers, which leads solely to the formation of the desired hetero-species. Even using an NMR equipped with a highly sensitive cryoprobe, proton signals from the original homo-dimers remain undetectable in solution. The 2D ROESY NMR spectrum (Fig. 2h) shows a clear crosscorrelation between the N,N-dimethylamino substituent of **VNMe**₂ and the phenyl group of **VH**. This indicates the close proximity of the two guest molecules and explicitly confirms formation of hetero-dimers, which simultaneously contain one VNMe2 and one VH complexed with two CB[8] macrocycles.

We then applied our strategy to generate hetero-dimers

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using extended BAP derivatives in order to obtain discrete chromophore coupled dimers. The extened BAP derivative Np14NMe₂, containing a 1,4-naphthyl core and bulky dimethylamino end-groups, can be mixed with Np14H and CB[8] to quantitatively produce the hetero-dimer product (Fig. S7-S9). While quantitative hetero-dimer is formed, the use of NMe₂ as an end-group led to complete quenching of 1,4-naphthyl fluorescence upon photoexcitation on account of photoinduced electron transfer. This was readily overcome by exchanging NMe₂ for an isopropyl moiety (CMe₂) yielding Np14CMe₂. A previous photophysical study^[36] showed that the self-recognition product of Np14CMe2 with CB[8] (i.e. homo-dimer, AA) is substantially suppressed due to its bulky end-groups, thus, suggesting Np14CMe₂ may be a better candidate to generate pure hetero-dimers with Np14H. Indeed, an equimolar mixture of Np14CMe₂ and Np14H with two equivalents of CB[8] instantaneously leads a quantitative self-sorting of hetero-dimers at equilibrium (Fig. S10-S13).

Strictly speaking, the complex of Np14CMe2 and Np14H does not represent a hetero-chromophore dimer as their central cores are identical. Therefore, we synthesized additional extended BAPs Ant910H and Ant910CMe2 using a 9,10-anthracenyl group as the central chromophore, which is also one aryl unit in width. Fig. 3b shows the proton spectrum for the equilibrium mixture of Np14CMe₂, Ant910H, and CB[8] with a molar ratio of 1:1:2. Only one set of CB[8] protons is observed with a splitting pattern typical for 2:2 complexation, which is further confirmed by a diffusion constant of $1.98 \times 10^{-10} m^2/s$ measured by DOSY NMR, exhibiting a typical value for a complex containing two CB[8] macrocycles (Table S1).[34,36,59] Variable-temperature NMR measurements (Fig. S15) display a gradual signal broadening and eventual coalescence of the pyridinium protons in Ant910H as the temperature increases from 278 to 317 K. This corresponds to restricted intra-complex rotation of the central anthracenyl moiety with an intermediate rate related to the NMR timescale.^[18,36] NOESY NMR offers definitive evidence for proximal stacking the two different chromophore moieties. In particular, clear correlations between the isopropyl group of Np14CMe₂ and the phenyl group of Ant910H (Fig. 3d) confirm successful formation of CB[8]-directed hetero-chromophore complexation. The desired heterospecies was observed by direct injection of the complex solution into ESI-MS using nanospray ionization, showing complex ion peaks with four positive charges (z=4) and a m/zratio centered around 916 (Fig. 3e), perfectly consistent with the m/z for [Np14CMe₂•Ant910H•CB[8]₂]⁴⁺. Importantly, swapping the end-groups of the two extended BAPs (i.e. Np14H and Ant910CMe₂) also leads to the desired complementary hetero-dimer. (Fig. S19-S23)

NOESY NMR (Fig. S17) indicates that 1,4-naphthyl and 9,10-anthracenyl chromophores are forced to stack on top of each other with a spacing of approximately 4 Å, as limited by the CB[8] cavity.^[22,23,60] Moreover, the pseudo-

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static nature of the discrete CB[8] dimer combined with its observed restricted intra-complex motions gives rise to a self-assembled system poised to exploit long-lived heterochromophore coupling with efficient energy transfer.



Figure 4 a) Discrete monomers and dimers of Np14CMe₂ or Ant910H can be generated through complexation with CB[7] and CB[8], respectively. b - e) Steady-state spectra for monomeric or dimeric species of Np14CMe₂ (green) and Ant910H (orange) and their physical (black) and mathematical mixtures (red, dashed). All solutions were excited at their isosbestic point (401 nm for CB[7] and 420 nm for CB[8]) in order to ensure an equal distribution of photons into both chromophores. The energy transfer efficiency was estimated by comparing the naphthyl emission at 485 nm between the mathematical and physical mixtures. Absorption: solid lines; emission: dotted lines with filled color. The Cl⁻ counterions are omitted for clarity.

Energy transfer in a supramolecular system can be readily investigated through steady-state spectroscopic measurements.^[61,62] For instance, the complexation of one equivalent of either **Np14CMe₂** or **Ant910H** with two equivalents of CB[7] generates discrete monomers in aqueous solution (Fig. 4a, Fig. S24).^[34,36] Their steady-state spectra in Fig. 4c shows that the superposition (the mathematical "mixture") of both monomers' spectra (Fig. 4b) resulting in absoroption and emission profiles identical to those recorded for their 50/50 physical mixture. This indicates that the two discrete monomer complexes behave independently in a mixed solution and that no energy transfer takes place between naphthyl and anthracenyl chromophores upon photoexcitation.

50/50 physical mixture of CB[8]-mediated A Np14CMe₂ and Ant910H homo-dimers yields heterochromophore dimers quantitatively, whose emission spectrum (Fig. 4e) is significantly different from that of their mathematical mixture. The emission intensity around 490 nm (from 1,4-naphthyl chromophore) is substantially reduced in the hetero-dimers, suggesting the existence of a fast non-radiative pathway to quench the photoexcitated naphthyl chromophore. On the other hand, emission of the 9,10-anthracenyl chromophore at 650 nm mainly stems from the excitation around 400 nm (Fig. S25), which is identical to the absorption band of the 1,4-naphthyl moiety. This suggests that non-radiative energy transfer takes place from the photoexcited naphthyl moiety to its neighboring anthracenyl group in the discrete hetero-dimer with an extremely high efficiency estimated to be > 85 %. The nature of this observed energy transfer (short- and/or long-ranged) is of great importance for the design of future systems, which is currently being investigated with time-resolved techniques.

In summary, we developed a straightforward supramolecular strategy based on CB[8]-directed dimerization to prepare hetero-chromophore dimers by simply mixing two precusors. The challenge of quantitatively forming hetero-dimers without other equilibrium by-products is overcome through self-sorting favored by the introduction of designed shape-complementary moieties. The resulting pseudo-static hetero-dimers enables strong, long-lived coupling between chromophores, which leads to efficient energy transfer upon photoexcitation. Using this supramolecular strategy, which is superisingly flexible and validated by five cases here, a broad range of discrete chromophore dimers can be readily prepared, beneficial to further investigation and understanding of exciton coupling. Moreover, the non-covalent nature of these assemblies facilitates optimal overlap between desired chromphores, providing alternative tectons for the development of high-performance optoelectronic materials through self-assembly.

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4

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Quantitative Formation of Hetero-dimers

Guanglu Wu, Zehuan Huang, Oren A. Scherman

Quantitative Supramolecular Hetero-dimerization for Efficient Energy Transfer

Quantitative generation of hetero-chromophore dimers through a straightforward supramolecular approach, enabling efficient interchromophoric energy transfer.

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