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Synthesis and characterization of porphyrin–DNA constructs for the self-assembly of modular energy transfer arrays

Modular energy transfer arrays are constructed using a DNA platform and CuAAC click chemistry. A central porphyrin molecule allows for up to four DNA arms to be attached through click chemistry. Onto these arms, complementary DNAs modified with energy donor dyes can be self-assembled.

As featured in:
Synthesis and characterization of porphyrin–DNA constructs for the self-assembly of modular energy transfer arrays†

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In this report, a 5′ azide-terminated single-stranded DNA (ssDNA) was covalently attached to a Zn-tetra(phenylethynyl)porphyrin (ZnTPEP) utilizing copper(1) catalyzed azide–alkyne cycloaddition (CuAAC) to form five DNA–porphyrin adducts containing one to four ssDNAs attached around the porphyrin core. The newly synthesized DNA–porphyrin adducts provide a modular platform that allows us to assemble donor–acceptor energy transfer (EnT) arrays/constructs using complementary dye-labeled ssDNAs, herein a 3′ AlexaFluor 546 (A546)-labeled ssDNA, with different donor:acceptor ratios. The photophysical properties of the DNA–porphyrin constructs, along with the individual donor and acceptor fluorophores, were investigated by electronic absorption and steady-state emission spectroscopy. The data shows that A546 (donor) emission spectrum is significantly quenched in each of the constructs with EnT efficiencies that are comparable to the predicted EnT determined through modeling the Förster resonance energy transfer (FRET) mechanism.

Introduction

Research into the use of molecular components for photo-voltaic and artificial photosynthetic devices has been ongoing for many decades. Generally, these systems attempt to mimic many of the photochemical and catalytic processes found in the natural photosynthetic systems of green plants and cyanobacteria by combining discrete systems to handle the various photo- and electrochemical processes of light absorption, energy transfer, charge separation, and chemical catalysis.1–3 Employing molecular arrays for solar energy conversion relies on the ability to specifically and reliably position and orient chromophores with sub-nanometer (nm) scale precision in order to maximize energy transfer (EnT). However, this can prove technically difficult when multiple synthetic steps are involved to position donor and acceptor chromophores within the nanoscale distances required, especially for multi-component light harvesting arrays requiring long-range EnT systems like those occurring naturally.4,5

DNA, normally serving as the hereditary material in almost all organisms, has been recently used to form a variety of 2D6,7 and 3D8–10 lattices by taking advantage of its loyal base-pairing recognition (A with T and C with G), and programmable nature, related to both base sequence and oligonucleotide length. Moreover, DNA, either in a simple double-stranded DNA (dsDNA) format or in self-assembled molecular frameworks, has been demonstrated capable of controlling spatial arrangements of external ligands11,12 and organic fluorophores13–32 with nanometer precision. Additionally, a large selection of fluorophore-labeled DNA oligonucleotides can be readily produced using automated DNA synthesizer via phosphoramidite chemistry.33 Thus, using sequence and length programmed vanilla- and fluorophore-labeled DNA provide a unique strategy to position chromophores within an EnT array with 3.4 Å resolution through directed DNA hybridization self-assembly. A major advantage of this approach is each DNA–chromophore conjugation reaction can be carried out individually prior to the self-assembly of the full EnT cascade. This limits the need for complex and often low-yielding protection and deprotection steps used in organic synthesis based EnT array construction. DNA-templated modular systems, on the contrary, allow for the straightforward fine-tuning of the position and orientation of different chromophores to conveniently form various EnT cascades through self-assembly.

Porphyrins are widely used chromophores in the design of artificial EnT systems because of their similarity to chlorophylls found in naturally occurring systems as well as their relative...
ease of synthesis and modification to tune the photophysical and redox properties. Porphyrins typically have strong, localized absorption bands in the blue and red regions of the solar spectrum. However, they lack absorptivity in the rest of the visible spectrum, especially the green region ($\lambda = 450–550$ nm). The lack of absorption for the porphyrin in this region allows for the selective excitation of donor chromophores, including A546, to examine EnT processes in the arrays. Herein, we present an analog of a natural light-harvesting complex by employing a DNA oligonucleotide as a molecular scaffold in spatially positioning donor and acceptor chromophores in a highly controlled manner. Specifically, 5,10,15,20-tetra(4-ethylphenyl)porphyrin Zn(II) (ZnTPEP) was used as an acceptor chromophore as well as a central attachment point to covalently bind one to four ssDNA via copper(i) catalyzed azide–alkyne cycloaddition (CuAAC). The resulting 1,4-substituted 1,2,3-triazole linkage between ZnTPEP and the 5′-azide terminated ssDNA (N$_3$-DNA) offers a versatile and modular scaffold for assembling EnT arrays (Fig. 1). DNA–porphyrin adducts have been synthesized previously by a variety of methods and some were used to study EnT processes. Compared to the previous study, the system presented in this report provides the unique function of a porphyrin (ZnTPEP) molecule both as an acceptor chromophore and as a central anchoring point of EnT arrays. The ease of adapting the system to study alternate dye positioning (e.g. two different donor-acceptor FRET pairs are investigated herein) or diverse sets of chromophores shows that this DNA-templated modular system is a useful platform for studying various EnT pairs. The successful synthesis of these DNA–porphyrin constructs provides a major building block (Fig. 1)
block with which larger arrays, forming longer-range EnT systems and featuring any group of chromophores, can be created through self-assembly of multiple complementary ssDNAs.

Results and discussion

Design of DNA–porphyrin constructs

A 13-nucleotide (nt) long DNA strand (N2-DNA, 5′-N3 CAC GGA CGC CTA C-3′) was designed to attach to a central meso-tetraphenylporphyrin (ZnTPEP) via CuAAC coupling chemistry to form a series of porphyrin–DNA “scaffolds” (Fig. 1). ZnTPEP provides both a structural component, arranging between one to four ssDNA strands around the porphyrin core, and an EnT acceptor chromophore for donors such as AlexaFluor 546 (A546). Two different complementary ssDNAs were designed with A546 attached at the 3′ position. When complexed with the porphyrin–DNA “scaffolds,” the A546 donor will be located at varying distances from the ZnTPEP acceptor. The first locates the donor as close as possible to the ZnTPEP by placing the A546 donor (5′-GGC GTC CGT G-3′-A546) at the terminus of the DNA duplex (A546-Terminal, A546-T, Fig. S1, ESf) while the second complementary ssDNA shifts the A546 donor five DNA bases away from the ZnTPEP acceptor (5′-GTA GGC GTG 3′-A546, A546-S, Fig. S1, ESf). For the second set, a 5-nt long ssDNA (5′-CGG TG-3′) is annealed along with A546-S when hybridizing with the “scaffold” to form a rigid 13-base pair (bp) long dsDNA. Formation of such dsDNA prevents variations in the distance of the donor–acceptor chromophore pair beyond the intended separation distance. Molecular modeling of the fully assembled arrays, using the MMFF94x force field, predicted a center-to-center distance between chromophores of 4.3 and 5.0 nm for A546-T and A546-S respectively (Fig. 1 and Fig. S1, ESf).

Synthesis and characterization of DNA–porphyrin adducts

The top of Fig. 1 shows the synthetic scheme of five 1,2,3-triazole linked DNA–porphyrin adducts (1-Arm, cis-2-Arm, trans-2-Arm, 3-Arm, and 4-Arm) using CuAAC coupling. Two equivalents of ZnTPEP were reacted with N2-DNA using CuAAC conditions adapted from other reports.37,38 We found that using the water soluble bathophenanthroline disulfonate Cu stabilizing ligand,48 as compared to tris[1-benzyl-1H-1,2,3-triazol-4-yl]methylamine (TBTA),49,50 provided a higher yielding and faster reaction. The quicker reaction (5 vs. 8 hours for TBTA) helps to minimize the Cu catalyzed oxidative degradation of DNA oligonucleotides.51 By using sub-stoichiometric amounts of N2-DNA, we insure that all five isomers of the porphyrin–DNA complex are synthesized in significant quantities.

Following the DNA porphyrin coupling reaction, the mixture of DNA–porphyrin adducts was purified by reverse phase HPLC (RP-HPLC). The eluted fractions containing different DNA–porphyrin adducts were then collected, concentrated, and stored at −20 °C. No insertion of copper into the porphyrin center was observed according to electronic absorption spectra (vide infra). Chromatograms of the isolated reaction mixture, recorded at both 260 nm (DNA absorption) and 425 nm (ZnTPEP Soret absorption), shows seven major peaks eluted at increasing concentrations of acetonitrile (Fig. 2A). The first peak, observed at 260 nm in the chromatogram at 23% acetonitrile, is attributed to a small amount of unreacted or degraded N2-DNA and other UV absorbing compounds in the reaction solution such as N-methyl-2-pyrrolidone (NMP) and bathophen. The last peak, observed absorbing only at 425 nm and eluted at 100% acetonitrile, contains unreacted ZnTPEP. The recovered samples correlated with each of other major peaks between 33% and 62% acetonitrile contain both DNA and porphyrin molecules. These correspond to ZnTPEP with four covalently attached ssDNA arms (4-Arm, 18.0% yield), three arms (3-Arm, 17.0%), two arms in the cis orientation (cis-2-Arm, 4.0%) or in the trans orientation (trans-2-Arm, 21.2%), and a single ssDNA arm (1-Arm, 39.8%), respectively. The relative amount of porphyrin to DNA absorption increases throughout the HPLC process due to the increasingly non-polar character of the ssDNA adducts. This is in agreement with the predicted polar nature of ssDNA as the greater number of attached DNA arms increases the polarity of the DNA–porphyrin adducts and therefore reduces retention time in the nonpolar stationary phase of the column. The two 2-Arm products were separated via HPLC due to different polarities between the cis- and trans-2-Arm conjugates, with the cis-2-Arm (at 44% acetonitrile) having a larger dipole moment than that of the trans-2-Arm (at 47% acetonitrile). Eluted HPLC fractions were further characterized by denaturing polyacrylamide gel electrophoresis (PAGE), confirming good separation and high purity of each of the five DNA–porphyrin adducts recovered from the HPLC purification (Fig. 2B).

To further confirm the formation of each individual DNA–porphyrin adduct and particularly which of the 2-Arm products is the cis- or trans-stereoisomer, we have tagged each of the DNA–porphyrin adduct with 5 nm gold nanoparticles (AuNPs) via a thiolated ssDNA (5′-thiol-GTA GGC GTG 3′, T-DNA) complementary to the “scaffold” DNA. AuNPs were attached to T-DNA through thiol-gold coupling as previously described37 and self-assembled to the scaffold. Based on the TEM (transmission electron microscopy) images of these AuNP–DNA–porphyrin hybrids (Fig. 3), the predicted cis-2-Arm DNA–porphyrin adduct (based on HPLC) gives the shorter average distance (1.0 nm)
between two adjacent AuNPs compared to the inter-particle distance in trans-2-Arm–AuNP sample (2.1 nm). This agrees with the molecular models also shown in Fig. 1. Herein, we need to point out that all the average inter-AuNP distances obtained by TEM on AuNP–DNA–porphyrin hybrids (adduct: cis, trans in nm; 2-Arm: 1.0, 2.1; 3-Arm, 1.5, 3.9; and 4-Arm: 1.5, 6.2) are much shorter than their theoretical values (cis: 12.2 nm and trans: 16.3 nm) calculated based on the dimensions of the dsDNA, porphyrin, and the organic compound linkers (shown in Fig. 1). The observation, however, is expected since it has been demonstrated that organic molecules shrink and deform dramatically under the high vacuum condition (less than $1.0 \times 10^{-5}$ Pa) required for TEM imaging.\textsuperscript{37} cis- and trans-distances can be seen to increase with increasing numbers of AuNPs due to steric of the complex as well. Nevertheless, the TEM images of the AuNP–DNA–porphyrin hybrids are consistent with the assignment of cis-2-Arm or trans-2-Arm stereoisomers isolated using HPLC, as well as 3-Arm and 4-Arm. Data has been summarized in Table 1.

**Electronic absorption spectra.** Fig. 4A shows the absorption spectra for each of the DNA–ZnTPEP adducts in 1× TAE buffer. Increasing the number of attached DNA strands through the 1,2,3-triazoles results in a slight red-shift of 1–4 nm, ranging from 431 nm in 4-Arm to 427 nm in 1-Arm, of the porphyrin Soret and Q-band peaks as previously reported due to the electron withdrawing effect of the triazole linkage on the meso-phenyl rings of ZnTPEP.\textsuperscript{52} The Soret peak for 1-Arm is significantly broader as compared to the other adducts, suggesting the porphyrins are behaving differently in the aqueous buffer than expected. Additions of organic solvents to solutions of 1-Arm interfered with DNA duplex formation with A546-T and A546-S. Solubility of the DNA–ZnTPEP adducts with two or more arms improves as overall polarity of the molecules increases solubility in aqueous solution.

Each of the DNA–ZnTPEP adducts were then self-assembled, through thermal annealing, to stoichiometric amounts of one of the complementary A546-tagged ssDNAs (A546-T or A546-S). Formation of such dsDNA of A546-ssDNA and DNA “scaffold” results in positioning the donor and acceptor chromophores close to the Förster distance of the donor–acceptor pair (vide infra). The absorbance of adducts duplexed with A546-T or A546-S can be seen in Fig. 4B and Fig. S3 (ESI\textsuperscript{†}), respectively, with absorbance of the A546 donor at 555 nm partially overlapping the Q-band absorbance of ZnTPEP at 560 and 605 nm. However, the absorption spectrum of ZnTPEP shows limited absorption between 450 and 530 nm, allowing selective excitation of the A546 donor chromophore at 520 nm for examination of EnT processes.

**Steady-state emission and energy transfer analysis.** Fig. 5 shows the absorption spectra of A546 (solid blue line) and ZnTPEP (solid red line), along with the emission spectrum of A546 scaled by its quantum yield of 0.83 ± 0.041 (dashed blue line). The emission of A546 has excellent spectral overlap with the Q-band absorptions of ZnTPEP, yielding an average integrated overlap ($J(\lambda)$) of $7.9 \times 10^{14}$ M$^{-1}$ cm$^{-1}$ nm$^{-1}$ (Table S1, ESI\textsuperscript{†}).

Utilizing Förster theory,\textsuperscript{53} the spectroscopic data can be used to estimate the efficiency of EnT between A546 donor and ZnTPEP acceptor. Eqn (1) provides an estimate of the Förster radius ($R_0$) in nm

$$R_0 = 8.79 \times 10^{-6}[k^2n^{-4}Q_{\text{d}}J(\lambda)]$$

where $k^2$ is the orientation factor between the transition dipole moments of the donor and acceptor, n is the refractive index, and $Q_d$ is the quantum yield of the A546 donor, calculated to be 0.83 ± 0.041 in this study (Fig. S7, ESI\textsuperscript{†}), and $J(\lambda)$ is the overlap integral. $k^2$ was assumed to be 2/3 for these arrays due to the

**Table 1** Measured distances and standard deviations between AuNPs of ZnTPEP–DNA–AuNP conjugates displayed in Fig. 3. All values in units of nanometers

<table>
<thead>
<tr>
<th>Inter-particle distance</th>
<th>cis-2-Arm</th>
<th>trans-2-Arm</th>
<th>3-Arm</th>
<th>4-Arm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) cis-</td>
<td>1.0 ± 0.2</td>
<td>1.5 ± 0.6</td>
<td>1.5 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>(b) trans-short axis</td>
<td>2.1 ± 0.3</td>
<td>3.9 ± 0.7</td>
<td>3.0 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>(c) trans-long axis</td>
<td></td>
<td>6.2 ± 1.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3 TEM images of different DNA + ZnTPEP adducts after hybridization with two (A and B), three (C), or four (D) 5 nm AuNP-conjugated complementary ssDNAs. All scale bars indicate 5 nm. Images displayed on the top of each panel are models displaying the idealized image of the AuNPs attached to the DNA + ZnTPEP adducts and include the distances measured for Table 1.
flexible nature of the alkyl linkers connecting A546 and ZnTPEP to the DNA chains pictured in Fig. S1 (ESI†). The Förster radii, calculated via eqn (1) for the five arrays ranged from 4.3 to 4.7 nm, are shown in Table S1 (ESI†) along with J(λ) for each of the dye pairs. Molecular modeling of the arrays predicts both the A546-T and A546-S donors to be near the Förster radii at 3.6 and 4.9 nm respectively (Fig. S1, ESI†). The predicted efficiency of EnT (E_{EnT}) can then be calculated using eqn (2).

\[
E_{EnT} = \frac{R_0^6}{R_0^6 + r^6}
\]  

where \(r\) is the distance between the center of the donor-acceptor pair extracted from modeling (3.6 nm for A546-T-ZnTPEP and 4.9 nm for A546-S-ZnTPEP). The predicted \(E_{EnT}\) values for arrays ranged from 75–78% for A546-T and 31–35% for A546-S (Table 2). Differences in theoretical \(E_{EnT}\) between samples are due to slight variations in molar absorptivity and therefor \(J(λ)\).

The emission spectra of A546-T and each of the five arrays are shown in Fig. 6. Emission spectra for A546-S and the corresponding arrays are shown in Fig. S4 as well as excitation spectra in Fig. S5 and S6 (ESI†). The complexes were excited at 520 nm where only A546 has significant absorption (see Fig. 4). The emission spectra of the arrays are significantly quenched with respect to A546 alone, which is consistent with an EnT mechanism to the ZnTPEP acceptor. The degree of quenching appears to increasing proportionally with the number of A546 donors. Unfortunately, due to the significantly higher quantum yield of A546 (0.83 ± 0.03) as compared to ZnTPEP (ranging from 0.032 ± 0.0003 for 4-Arm to 0.0075 ± 0.00008 for 1-Arm) which were each calculated by the comparative method\(^{54}\) in 1× TAE-Mg\(^{2+}\) buffer and can be seen in Fig. S7 (ESI†), the emission spectra of the latter is effectively obscured by A546 emission and cannot be used as a confirmation of EnT. Quenching of A546 emission due to EnT was confirmed by measuring the fluorescence spectra over a range of temperatures. Upon heating above the melting temperature for the dsDNA, the A546 emission returned to its unquenched levels, consistent with a complete separation of the fluorophores. After cooling and reassembling of the arrays in a temperature controlled cell, the emission of A546 was quenched significantly to the same level as in the fully assembled arrays (Fig. S8, ESI†).

The experimental values of \(E_{EnT}\) where calculated via eqn (3),

\[
E_{EnT} = 1 - \frac{I_{DA}}{I_D}
\]

where \(I_{DA}\) is the integrated fluorescence of the A546 in the fully assembled array and \(I_D\) is the integrated fluorescence of A546.

Table 2  Experimental (and theoretical) EnT efficiencies of the two sets of donor-acceptor arrays. Experimental error ±5%.

<table>
<thead>
<tr>
<th></th>
<th>4-Arm</th>
<th>3-Arm</th>
<th>cis-2-Arm</th>
<th>trans-2-Arm</th>
<th>1-Arm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A546-T</td>
<td>87% (77%)</td>
<td>87% (78%)</td>
<td>72% (74%)</td>
<td>85% (76%)</td>
<td>75% (75%)</td>
</tr>
<tr>
<td>A546-S</td>
<td>42% (35%)</td>
<td>44% (35%)</td>
<td>36% (31%)</td>
<td>49% (33%)</td>
<td>31% (32%)</td>
</tr>
</tbody>
</table>

Fig. 4  Electronic absorption spectra of the DNA–ZnTPEP adducts (A) and fully assembled EnT arrays combining the DNA–ZnTPEP adducts with equimolar amounts of A546-T (B).

Fig. 5  Absorption spectra of A546 (solid blue line) and the Q bands of 1-Arm (solid red line). Emission of A546 is also shown (dashed blue line) scaled by the quantum yield (0.83 ± 0.041) relative to the molar absorptivity of the molecule. The overlap integral \(J(λ)\) is shown as the shaded purple region.
alone. The experimental and theoretical EnT efficiencies are shown in Table 2. The distance between donor and acceptor has a large effect on the overall experimental EnT, as predicted by the Förster equations, with the A546-T–ZnTPEP samples having a higher EnT efficiency than the related A546-S–ZnTPEP donor–acceptor pairs. However, almost all of the experimental efficiencies are greater than the theoretical.

Variations between theoretical and experimental $E_{\text{EnT}}$ can be attributed to the possibility of movement and rotation of the chromophores through the alkyl linkers between the duplexed DNA and both A546 and ZnTPEP. As was studied previously by Albinsson and co-workers,55 fluorophores covalently attached to DNA by flexible alkyl linkers have a range of positions they can occupy and therefore the distance between the donor and acceptor dyes can vary significantly. Using time-resolved FRET measurements and molecular dynamics simulations, they described how the positions of the fluorophores can be modeled as roughly Gaussian distributions with the maximum probability occurring where the strain on the alkyl linker and steric interference from the DNA duplex are minimal. Through the MD simulations, they place the potential positions for the dyes and linkers within 24% of the median value. Considering the linking group used in our work is very similar to this report, it can be anticipated that the A546 dyes extend approximately perpendicular to the axis of the rigid DNA duplex, but with a range of configurations. The predicted positions, based on MMFF94x geometry optimized structures, of 1-Arm–(A546-T) and 1-Arm–(A546-S) are displayed in Fig. S1 (ESI†) as well as the potential minimum and maximum donor–acceptor distances in Fig. S2 (ESI†). If we extrapolate the previous MD results to our system, we can expect a range of distances for the A546-T–ZnTPEP arrays to be 3.6 ± 0.86 nm and A546-S–ZnTPEP arrays to be 4.9 ± 1.2 nm. The experimentally derived $E_{\text{EnT}}$ values shown in Table 2 are reasonably close to theoretically determined values assuming a distribution of A546 positions near the median donor–acceptor distance. As also discussed by Albinsson and co-workers,55 the distance between dye molecules on the structure has a greater effect on the theoretical energy transfer than the orientation factor, $\kappa^2$. For this reason along with the ability for the alkyl linkers to freely rotate in solution, $\kappa^2$ is considered 2 in our calculations.

Additional experimental deviations from theoretical calculations can be attributed to increasing possible EnT pathways through homo-FRET, which increases overall EnT efficiency in the DNA–porphyrin array. It has been previously reported that positioning multiple donor chromophores near an acceptor allows for the possibility of homo-FRET between donors and leads to higher end-to-end EnT efficiency of the system.56 Provided the donors have a relatively small Stokes shift, leading to a high overlap integral $J(\lambda)$, and they are positioned relatively close to each other, homo-FRET can compete with EnT from donor to acceptor. This process is known to extend the donor fluorescence lifetime and increase the overall donor-acceptor EnT efficiency. We hypothesized that increasing the number of A564 donors on going from 1-Arm to 4-Arm would allow homo-FRET to occur and lead to higher overall EnT efficiencies. We estimated the overlap integral, $J(\lambda)$, of 3.4 × 10$^{15}$ M$^{-1}$ cm$^{-1}$ nm$^4$ for A546 absorbance and emission, leading to a Förster radius, $R_0$, of 5.7 nm. This value is close to the separation of A546 molecules modeled in these arrays at 5.0 and 7.2 nm for A546-T and A546-S respectively. Calculating the theoretical homo-EnT between A546 donors using eqn (1) and (2) gives expected $E_{\text{EnT}}$ of 69% and 19% in A546-T–ZnTPEP and A546-S–ZnTPEP arrays, respectively. This relatively high level of $E_{\text{EnT}}$ for homo-FRET can help to account for the higher efficiency for the 3-Arm and 4-Arm constructs, especially in the A546-T array.

In order to improve end-to-end $E_{\text{EnT}}$, future architectures of similar porphyrin–DNA arrays could be designed with shorter, more rigid chromophore linkers. Shorter linker regions improve EnT twofold: both in reducing distance between chromophores as well as lessening the ability for the molecules to tumble and vary in both distance and orientation, which can be seen to increase theoretical efficiency in eqn (1) and (2). Our currently planned future work includes forming a long-range EnT system building from the core N$_2$-DNA–ZnTPEP scaffold. Extending the strand complementary to N$_2$-DNA allows space for multiple energy donors to be self-assembled onto the array. Multi-step EnT to direct energy to the centralized ZnTPEP is then possible over a long range.

### Conclusion

In this paper, DNA was successfully used as a scaffold to form two unique sets of five donor–acceptor EnT arrays that contain 1–4 A546 donors self-assembled to a ZnTPEP acceptor. CuAAC reactivity was employed to attach the ssDNA on which the array could assemble through thermal annealing and each adduct was separated through HPLC purification and verified through PAGE and TEM analysis. Photophysical characterization is consistent with modeled Förster resonance energy transfer from...
the A546 donors to the ZnTPEP acceptor while also accounting for homo-FRET between A546 donors. The A546 singlet excited state emission is quenched in each of the arrays, leading to EnT efficiencies of over 85%. These array systems demonstrate the ability to use DNA and a central porphyrin molecule to form an easily modifiable, modular structure that can potentially be used for facile construction of complex and highly efficient long-range model energy transfer systems for solar energy conversion and artificial photosynthesis.

Conflicts of interest
There are no conflicts to declare.

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