

UC Riverside

UC Riverside Previously Published Works

Title

Complementary Lock-and-Key Ligand Binding of a Triplet Transmitter to a Nanocrystal Photosensitizer

Permalink

<https://escholarship.org/uc/item/0v563725>

Journal

Angewandte Chemie International Edition, 56(20)

ISSN

1433-7851

Authors

Li, Xin
Fast, Alexander
Huang, Zhiyuan
et al.

Publication Date

2017-05-08

DOI

10.1002/anie.201701929

Peer reviewed

Nanocrystals

International Edition: DOI: 10.1002/anie.201701929

German Edition: DOI: 10.1002/ange.201701929

Complementary Lock-and-Key Ligand Binding of a Triplet Transmitter to a Nanocrystal Photosensitizer

Xin Li, Alexander Fast, Zhiyuan Huang, Dmitry A. Fishman, and Ming Lee Tang*

Abstract: Owing to the difficulty in comprehensively characterizing nanocrystal (NC) surfaces, clear guidance for ligand design is lacking. In this work, a series of bidentate bis(pyridine) anthracene isomers (2,3-PyAn, 3,3-PyAn, 2,2-PyAn) that differ in their binding geometries were designed to find the best complementary fit to the NC surface. The efficiency of triplet energy transfer (TET) from the CdSe NC donor to a diphenylanthracene (DPA) acceptor mediated by these isomers was used as a proxy for the efficacy of orbital overlap and therefore ligand binding. 2,3-PyAn, with an intramolecular N–N distance of 8.2 Å, provided the best match to the surface of CdSe NCs. When serving as a transmitter for photon upconversion, 2,3-PyAn yielded the highest upconversion quantum yield (QY) of $12.1 \pm 1.3\%$, followed by 3,3-PyAn and 2,2-PyAn. The TET quantum efficiencies determined by ultrafast transient absorption measurements showed the same trend.

The design of ligands for nanocrystals is challenging because the high surface area to volume ratio modifies the bulk lattice in ways that are difficult to predict.^[1] Ligand development requires an understanding of the binding mechanism(s), as well as the nature of the available binding sites. The latter is difficult to characterize,^[2] owing to the disordered nature of the organic–inorganic interface and the inherent distribution in the size and shape of colloiddally synthesized nanocrystals. Ligands that are structurally complementary to the nanocrystal surface are critical in enhancing exciton delocalization within the hybrid structure. Herein, we examine the consequence of subtle perturbations in the structure of ligands that serve as transmitters for triplet excitons from nanocrystal donors. Much like Fisher's lock-and-key mechanism for the binding of substrates to an enzyme active site,^[3] only one of the transmitter ligands complements the nanocrystal surface, resulting in a high photon upconversion quantum yield (QY) that arises from efficient triplet energy transfer (TET).

Conjugated organic ligands can drastically enhance energy transfer from a nanocrystal (NC) donor to an acceptor. This is especially evident in a hybrid complex consisting of NC sensitizers and acene annihilators. For example, a combination

of PbS nanocrystals and tetracene derivatives was shown to efficiently upconvert near-infrared into visible light under one sun conditions.^[4] In this process, low-energy photons harvested by the NCs are funneled through surface-anchored transmitters to free annihilators in solution. Two annihilators in their triplet excited state collide, converting two low-energy photons into one high-energy photon through triplet–triplet annihilation (TTA). In this hybrid system, triplet energy transfer (TET) from the NC to transmitter molecules is the bottleneck limiting the photon upconversion QY. Therefore, designing a transmitter ligand with a high binding affinity for the NC donor in a geometry that facilitates orbital overlap is crucial in increasing the rate and the overall quantum efficiency of TET.

A series of isomeric bidentate bis(pyridine) anthracene transmitter ligands were designed to simultaneously fulfill these two requirements (Figure 1 a). The bidentate nature of these transmitters implies that the anthracene core is parallel to the NC surface if the ligand binds via the two pyridine N atoms. This increases the orbital overlap between the NC donor and the acene acceptor, which is necessary for efficient Dexter energy transfer. In contrast, previous work solely involved monodentate transmitters with conjugated cores that could be either perpendicular to or parallel with the NC surface.^[4b,5] Pyridine (Py) was selected to lock the anthracene core in a fixed geometry because it is widely used as a coordination ligand in organometallic complexes.^[6] In

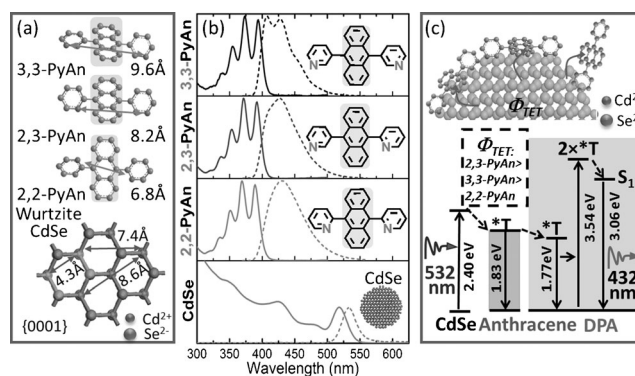


Figure 1. a) The distances between the pyridine N atoms in the three isomers are shown together with the {0001} facet of wurtzite CdSe NCs for which the distances between neighboring cations are given. b) Absorption and emission spectra of the three bis(pyridine) anthracene isomers and 2.4 nm diameter CdSe NCs. All spectra were measured in *n*-hexane at room temperature. c) Possible binding geometries and the energy transfer in this hybrid photon upconversion platform. The energy diagram depicts the triplet excitonic states of the CdSe NC, the anthracene transmitter, and the 9,10-diphenylanthracene annihilator.

[*] X. Li, Z. Huang, Prof. M. L. Tang
Chemistry, University of California, Riverside
501 Big Springs Road, Riverside, CA 92521 (USA)
E-mail: minglee.tang@ucr.edu

A. Fast, Dr. D. A. Fishman
Chemistry, University of California, Irvine (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<http://dx.doi.org/10.1002/anie.201701929>.

addition, Py shows a better binding affinity for the NC surface than the previously used carboxylic acid (COOH) group.^[7] Finally, both COOH and Py groups do not significantly quench the NC exciton or perturb NC photoluminescence, unlike thiols.^[8] This is important in minimizing losses in this TTA-based photon upconversion platform.

As shown in Figure 1 a, the three transmitters differ in the connectivity of the pyridines with the anthracene core. One isomer is unsymmetric, with one Py connected in the *meta* and the other in the *ortho* position (2,3-PyAn), while the other two isomers are exclusively linked at either the *meta* or the *ortho* positions (3,3-PyAn and 2,2-PyAn, respectively). The intramolecular N–N distances vary from 9.6 Å for 3,3-PyAn to 8.2 Å for 2,3-PyAn and 6.8 Å for 2,2-PyAn. The atomic scale differences between the pyridine groups provide the possibility that only one isomer might match the unique Cd²⁺–Cd²⁺ distances on the NC surface. As transmitter ligands for photon upconversion, the 2,3-PyAn isomer yielded the highest upconversion QY of 12.1 ± 1.3%, followed by 3,3-PyAn (8.1 ± 0.7%) and then 2,2-PyAn (2.5 ± 0.7%). Transient absorption (TA) measurements reflected the trends observed in the steady-state upconversion experiments, where the efficiency of TET is highest for 2,3-PyAn at 42.0% and lowest for 2,2-PyAn at 23.1%. From these results, we concluded that the 2,3-PyAn isomer best complements the wurtzite CdSe NC by “locking” to its surface. Figure 1 b shows the absorption and emission spectra for all three bis(pyridine) anthracene isomers and the 2.4 nm diameter CdSe NCs used in this study. The absorption spectra share similar features, being governed mainly by the anthracene core. However, from 3,3-PyAn to 2,3-PyAn to 2,2-PyAn, the absorption maximum shows a 4 nm blue shift, as observed in a related series of phenylpyridine isomers.^[9] Details of the synthesis can be found in the Supporting Information.^[10]

Steady-state photon upconversion measurements were conducted to evaluate the effect of the binding geometry on TET (see the Supporting Information, Figure S2 a). The energy diagram in Figure 1 c illustrates the overall upconversion process. TET from the NC to the bound anthracene transmitter is exergonic by roughly 0.57 eV. In order for upconversion to occur, TET must occur from the CdSe NC photosensitizer to a bound PyAn transmitter to a 9,10-diphenylanthracene (DPA) annihilator. The latter is commonly used in organic–organic upconversion schemes because of its long-lived, low-lying triplet state and relatively high fluorescence QY (90%).^[11] The upconversion QY in our study is defined as described in Equation (1),

$$\Phi_{\text{UC}} = 2\Phi_{\text{ref}} \frac{N_{\text{abs(ref)}}}{N_{\text{abs(sample)}}} \frac{N_{\text{em(sample)}}}{N_{\text{em(ref)}}} \quad (1)$$

where Φ_{UC} and Φ_{ref} are the QYs of the upconversion sample and reference, respectively. $N_{\text{abs/em(sample/ref)}}$ refers to the photons absorbed/emitted by the sample/reference.

The optimized upconversion QYs were found by varying the transmitter density on the NC surface (Figure S4).^[5c] The average number of bound anthracene ligands per CdSe NC, m , was determined by UV/Vis electronic absorption spectroscopy (see the Supporting Information for details). Under

optimized conditions, $m = 6.6$ and 7.8 for 2,3-PyAn and 3,3-PyAn, respectively, while for 2,2-PyAn, the average number of bound ligands per NC is six times greater with $m = 36.6$ (Table 1). The isolated CdSe/PyAn complexes were mixed with 2.1 mM DPA and excited with a 532 nm continuous wave (CW) laser with a power density of 12.7 W cm⁻². Rhodamine 6G in ethanol was used as the reference (see Figure S2 b and the Supporting Information for details).^[5c]

Table 1: The quantum yield of photon upconversion (Φ_{UC}), the TET efficiency (from both upconversion and TA spectroscopy, $\Phi_{\text{TET(UC)}}$ and $\Phi_{\text{TET(TA)}}$, respectively), and the average number of bound ligands per CdSe (m) for each CdSe/PyAn complex.^[a]

	2,3-PyAn	3,3-PyAn	2,2-PyAn
Φ_{UC} [%]	12.1 ± 1.3	8.1 ± 0.7	2.5 ± 0.7
$\Phi_{\text{TET(UC)}}$ [%]	25.8	17.3	5.34
$\Phi_{\text{TET(TA)}}$ [%]	42.0	38.1	23.1
m	6.6	7.8	36.6
t_{trap} [ps]	51.1	35.2	40.6
t_{q} [ns]	0.785	1.04	0.81
t_{TET} [ns]	0.785	1.05	0.80
k_{TET} [$\times 10^9$ s ⁻¹]	1.28	0.962	1.25

[a] Based on the TA data, analysis of the kinetics of the NC donor provides the decay time constants of surface trapping and quenching on the NC induced by the PyAn ligands, t_{trap} and t_{q} . Analysis of the kinetics of $T_{\text{L1}} \rightarrow T_{\text{Ln}}$ on the PyAn transmitters gives the time constant and rate of TET (t_{TET} and k_{TET} , respectively) from the CdSe NCs.

As the transmitter ligand shuttling triplet excitons from CdSe donors to DPA acceptors, 2,3-PyAn performed best out of all three bis(pyridine) anthracene isomers. The upconversion QY for 2,3-PyAn was as high as 12.1 ± 1.3%, comparable to the 14.3% record with 9-anthracenecarboxylic acid (9-ACA) as transmitter.^[5c] The excitation density (I_{th}) denoting the transition from the quadratic to the linear regime for this 2,3-PyAn transmitter is 146.8 mW cm⁻² for a 68.7 μM solution of functionalized CdSe NCs in 2.1 mM DPA in hexanes at room temperature. The upconversion QYs for the other two isomers, 3,3-PyAn and 2,2-PyAn, were 8.1 ± 0.7% and 2.5 ± 0.7%, respectively. Yanai, Kimizuka, and co-workers have shown that monodentate PyAn transmitters with just one pyridine moiety for binding to the NC result in an upconversion QY of 1.4%.^[12] This shows that at least two of the bidentate ligands here outperform their monodentate congener, probably by increasing orbital overlap with the CdSe NC donor. Although 3,3-PyAn and 2,3-PyAn have a similar binding affinity to wurtzite CdSe NCs, the upconversion QY of the latter is almost twice as large as that of the former. This indicates that its binding geometry matches the CdSe surface lattice best and tightly locks the anthracene core to the surface. While 2,2-PyAn may bind more strongly to the NCs (as indicated by a higher number of surface-bound ligands), the upconversion QY is low, quite close to that for the monodentate ligand. This suggests that 2,2-PyAn may bind to the surface in a monodentate fashion. This can also explain the higher number of surface-bound ligands as the monodentate geometry has a smaller footprint than the bidentate binding geometry, thus allowing the NC surface to accommodate more ligands.

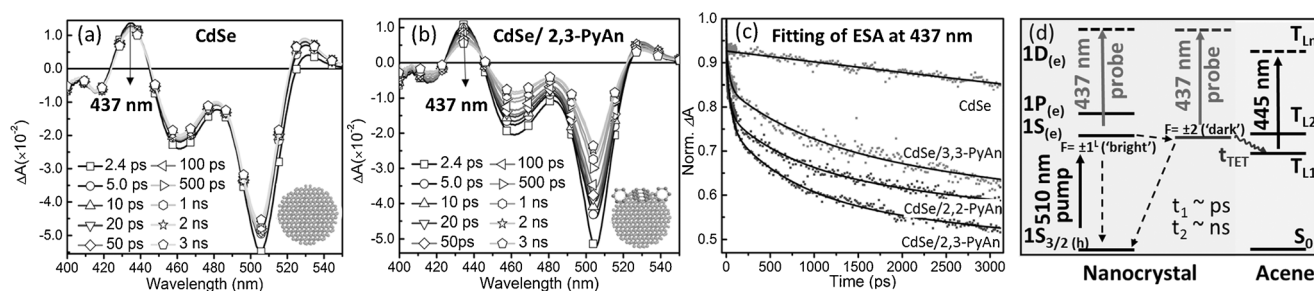


Figure 2. Femtosecond TA difference spectra in hexanes solution of a) CdSe NCs only and b) CdSe NCs with surface-anchored 2,3-PyAn. The CdSe NCs were selectively excited with a 505 nm 100 fs pulsed laser. Experimental delays span from 2.4 ps (black squares) to 3 ns (grey pentagons). c) Depletion of the CdSe excited-state absorption monitored by kinetic traces at 437 nm. The dots are the raw data from TA measurements for CdSe NCs only as well as CdSe NC/transmitter complexes with 3,3-PyAn, 2,2-PyAn, or 2,3-PyAn as the ligand. The black solid lines are the fits for each complex. d) An energy diagram depicting the physical processes during the TA measurements. The solid lines denote the pump and probe wavelengths, dashed lines denote the relaxation processes on the CdSe NCs, and wavy lines denote possible quenching processes induced by the ligand, such as triplet energy transfer (TET).

TA measurements were performed to determine the quantum efficiency of TET, $\Phi_{\text{TET(TA)}}$, and the rate of TET for each isomer. TA spectra were acquired for up to 3.1 ns for each CdSe/PyAn complex with the highest upconversion QY. The TA difference spectra of native CdSe NCs without ligand exchange and the CdSe/2,3-PyAn complex in the range of 400–560 nm are shown in Figure 2a and b, respectively. The complete TA difference spectra spanning the visible region for all three CdSe/PyAn complexes can be found in Figure S5. In all experiments, the pump laser power was low (220 nJ) such that no multi-exciton annihilation occurred. This was confirmed by power dependence experiments. All of the experiments were conducted in the linear regime (see Figure S6).

The transient kinetics of the excited state absorption (ESA) of CdSe NCs at 437 nm in Figure 2c reveal that the quenching of the NCs induced by the ligand is fastest for the 2,3-PyAn transmitter compared to the 3,3-PyAn and 2,2-PyAn isomers. As shown in Figure 2d, the ESA at 437 nm was assigned to transitions from band edge states $F = \pm 1^L$ (“bright”) and $F = \pm 2$ (“dark”) to higher-energy states on the CdSe NCs.^[13] Possible channels depopulating the ESA include electron trapping on defect sites, stimulated emission, and band edge recombination.^[13] The multiexponential model shown in Equation (2) was used to fit the kinetics.

$$\Delta A = \sum_{i=1}^n A_i \exp(-t/t_i) \quad (2)$$

Here, ΔA is the ESA for the CdSe NC, and A_i and t_i are the amplitude and corresponding decay constant for each component. For the unmodified CdSe NCs, two time constants, $t_1 = 1.05$ ps and $t_2 = 34.6$ ns, were needed for a satisfactory fit of the data. Considering the timescales, the fast decay may correspond to electron trapping to shallow defect sites on the surface or stimulated emission, and the slower decay may be due to direct band edge recombination, that is, $F = \pm 1^L$ (“bright”) $\rightarrow 1S_{3/2(h)}$.^[14] The time constants extracted are in good agreement with previous reports.^[14] Analysis of the ESA of the CdSe NC photosensitizers functionalized with pyridine bidentate ligands with a triexponential fit given the longest component fixed, yielded two other decay components with

similar timescales of about 40 ps and approximately 1 ns for all three ligands. We note that the fastest decay process, $t_{\text{trap}} \approx 40$ ps, is slower than that for the pristine CdSe NCs and may correspond to charge trapping to deeper defects that were created during ligand exchange and cleaning.^[14,15] This change is observed across all CdSe/PyAn complexes as the same functional group is involved. In the presence of a transmitter ligand, the new decay constant, t_q , with a timescale of approximately 1 ns, corresponds to an additional decay pathway introduced by surface-bound PyAn transmitters, which is most probably due to TET from $F = \pm 2$ (“dark” state on NC) to T_{L1} (the triplet state on anthracene) or other decay processes induced by the disruption of the original ligand shell. The values for t_{trap} and t_q are listed in Table 1 for each ligand. Detailed fitting parameters can be found in Table S2. As the solid line in Figure 2c shows, the fits are robust. Here, we focus on the depleted ESA of the NCs because its decay kinetics are directly related to the physical process of TET to surface-bound PyAn.

The kinetics of the triplet excited state formed on the PyAn transmitters can be monitored at 445 nm, an isosbestic point in the TA spectra. While the $T_{L1} \rightarrow T_{Ln}$ transition of anthracene is normally found around 433 nm, in this work, the ESAs of the transmitter and NC overlap, resulting in an isosbestic point at 445 nm. It is well known that the excited-state energy levels of anthracene are very sensitive to small changes in the molecular structure.^[16] Changes in the TA kinetics hypsochromic to this isosbestic point are dominated by ESA of the CdSe NCs, while difference spectra bathochromically shifted from 445 nm were assigned to the ESA of the triplet excited state on the anthracene ligand. The overall $T_{L1} \rightarrow T_{Ln}$ transition time decay constants at approximately 445 nm are 800 ps, 785 ps, and 1050 ps for 2,2-PyAn, 2,3-PyAn, and 3,3-PyAn, respectively. We notice that the decay time constant of the ESA at 437 nm of the nanocrystal photosensitizer in the CdSe/PyAn complexes (t_q) is inversely correlated to the growth in the absorption of the triplet excited states on the transmitters at 445 nm (t_{TET}). This constitutes strong evidence that the quenching on NC induced by PyAn is due to TET. Detailed fitting procedures are given in the Supporting Information (Figure S8). Using TA spec-

troscopy, Mongin and co-workers determined the k_{TET} value from CdSe NC to surface-bound 9-ACA to be about $2.0 \times 10^9 \text{ s}^{-1}$,^[5d] which is on the same order of magnitude as the value obtained in this study. Note that the average number of bound ligands, m , was about twelve in their case. Using time-resolved photoluminescence measurements, Piland and co-workers determined a rate of energy transfer of about $1.5 \times 10^7 \text{ s}^{-1}$ for a similar system, which is about two orders of magnitude smaller.^[17] This lower rate of TET is perhaps due to the lower number of surface-bound transmitter ligands (ca. 2). We have considered electron transfer from ligands to CdSe NCs as another possible energy transfer mechanism. However, the absence of peaks at 629 nm, 681 nm, and 748 nm for the anthracene radical cation^[18] or 596 nm and 732 nm for the anthracene radical anion,^[19] rules out the possibility of sequential charge transfer as a possible mechanism for TET for CdSe/PyAn complexes (see Figure S5).

The efficiencies of TET from NC to PyAn obtained from TA measurements, $\Phi_{\text{TET(TA)}}$, are 42.0%, 38.1%, and 23.1% for 2,3-PyAn, 3,3-PyAn, and 2,2-PyAn, respectively, correlating directly with the upconversion QYs. $\Phi_{\text{TET(TA)}}$ was extracted from the kinetics at 445 nm of the CdSe/PyAn complexes after accounting for the contribution of the NC (Figure 3; see also Figure S8). As expected, the 2,3-PyAn

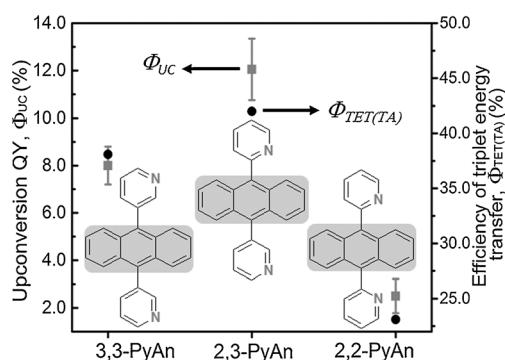


Figure 3. The TET efficiency measured by transient absorption spectroscopy, $\Phi_{\text{TET(TA)}}$ (black circles) for each bis(pyridine) anthracene transmitter correlates with the corresponding photon upconversion QY (gray squares).

isomer with the highest upconversion QY has the highest $\Phi_{\text{TET(TA)}}$ value, and it quenches the CdSe NC donor the fastest (lowest t_q). In addition, the 2,2-PyAn transmitter with the lowest upconversion QY has the lowest $\Phi_{\text{TET(TA)}}$. However, we noticed that 2,2-PyAn quenches the CdSe NC donor more effectively than the 3,3-PyAn isomer (Figure 2c and Table 1) despite the fact that it has a lower $\Phi_{\text{TET(TA)}}$ and upconversion QY. This observation is consistent with reports on the superlinear dependence of NC emission on ligand functionalization, and that NC photoluminescence can only be related to ligand binding at high surface coverage, and not at the low density of transmitter ligands in this work.^[7,20]

Another way of calculating the quantum efficiency of TET is by considering the photon upconversion QY obtained under CW irradiation, which is a convolution of the following factors in Equation (3).^[21]

$$\Phi_{\text{UC}} = \Phi_{\text{TET(UC)}} \Phi_{\text{TTA}} \Phi_{\text{A}} \quad (3)$$

Here, Φ_{UC} is the upconversion QY. $\Phi_{\text{TET(UC)}}$ is the efficiency of TET from CdSe to the bound bis(pyridine) isomers, Φ_{TTA} the efficiency of TTA for the DPA annihilator, and Φ_{A} is the fluorescence QY of DPA. If we assume $\Phi_{\text{A}} = 0.9$ and $\Phi_{\text{TTA}} = 0.52$ for DPA based on previous reports,^[11,22] the calculated $\Phi_{\text{TET(UC)}}$ values are 25.8%, 17.3%, and 5.3% for 2,3-PyAn, 3,3-PyAn, and 2,2-PyAn, respectively. Note that in our system, $\Phi_{\text{TET(UC)}}$ can be regarded as the overall TET efficiency and is composed of two individual TET steps, that is, TET from the NC light absorber to the PyAn transmitter, $\varphi_{\text{TET(NC} \rightarrow \text{PyAn)}}$, and from the PyAn transmitter to the DPA annihilator, $\varphi_{\text{TET(PyAn} \rightarrow \text{DPA)}}$, as shown in Equation (4):

$$\Phi_{\text{TET(UC)}} = \varphi_{\text{TET(NC} \rightarrow \text{PyAn)}} \varphi_{\text{TET(PyAn} \rightarrow \text{DPA)}} \quad (4)$$

Therefore, as the TA measurements only characterize the TET process from the NC to the surface-bound transmitters, $\varphi_{\text{TET(NC} \rightarrow \text{PyAn)}}$, it makes sense that $\Phi_{\text{TET(TA)}}$ is larger than $\Phi_{\text{TET(UC)}}$ (Table 1). However, $\varphi_{\text{TET(PyAn} \rightarrow \text{DPA)}}$ should be close to 1 as the concentration of DPA is 2.1 mM, and TTA is diffusion-limited here.^[17,23] The discrepancy may arise from the fact that the upconversion QY is measured in the presence of the annihilator whereas the φ_{TET} from TA is determined in the absence of the DPA emitter. The DPA annihilator is an energy sink for the triplets transferred to the PyAn transmitters and increases the efficiency of TET.

In conclusion, the binding geometry greatly affects the efficiency of TET from the NC to bound ligands. The best binding geometry results in a significantly higher upconversion QY, as reflected in the increased efficiency of TET given by TA measurements. This study indicates that even though the surface chemistry of NC is ill-defined and difficult to accurately predict, it is still oriented in a specific manner. Careful design of surface ligands to match the NC surface can maximize exciton delocalization between inorganic NCs and organic molecules. The use of bidentate ligands here suggests a new approach in the design of ligands for nanocrystal surfaces to maximize charge or energy transfer across these hybrid surfaces.

Acknowledgements

M.L.T. thanks the U.S. Army W911NF-16-1-0523 for instrumentation and CHE-1351663 for supplies and personnel. D.A.F. acknowledges NSF grant 1532125.

Conflict of interest

The authors declare no conflict of interest.

Keywords: anthracenes · bidentate ligands · CdSe nanocrystals · ligand design · upconversion

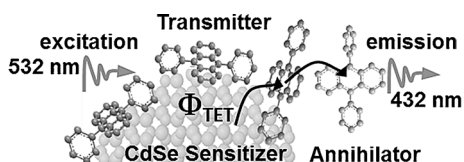
Communications



Nanocrystals

X. Li, A. Fast, Z. Huang, D. A. Fishman,
M. L. Tang* ————— ■■■■-■■■■

Complementary Lock-and-Key Ligand
Binding of a Triplet Transmitter to
a Nanocrystal Photosensitizer



Transmitter optimization: A series of bidentate bis(pyridine) anthracene isomers that differ in their binding geometries were designed to find the best fit to the surface of CdSe nanocrystals. The

efficiency of triplet energy transfer (TET) from the CdSe NC donor to a diphenylanthracene acceptor via these transmitters was used as a proxy for the efficacy of orbital overlap and ligand binding.