Photofunctional Self-Assembled Nanostructures Formed by Perylene Diimide–Gold Nanoparticle Hybrids †

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We report on the synthesis of organic dye-metal nanoparticle hybrids from two thiol-derivatized perylenediimide (PDI) ligands and 1.5 nm gold nanoparticles. The hybrids form spherical nanostructures when cast from 40% methanol/chloroform solution and toluene. The spherical aggregates are in the size range 50-230 nm in 40% MeOH/CHCl₃ mixture and 100-400 nm in toluene solution, as evidenced by transmission electron microscopy (TEM). Scanning electron microscopy (SEM) measurements show that these spherical aggregates are vesicles with a hollow interior. The π - π interactions of the perylenediimides are the predominant driving force leading to the aggregation of the hybrids, whereby the sizes of the nanospheres can be regulated via the PDI linker moiety and solvent choice. Femtosecond transient absorption studies of the hybrids reveal complex photophysical behavior involving electron transfer from the gold nanoparticles to the PDI moieties. This study shows that the formation of well-defined hybrid nanostructures as well as tuning their sizes can be achieved through employing a combination of the capping ligand choice and regulating the solvophobic interactions between the ligands.

Introduction

Self-assembly of metal nanoparticles has emerged as an important area of research due to potential applications in sensors,¹ catalysis,² and electronics.³ It has been demonstrated that the size, shape, and complexity of the building blocks are very important in determining the self-assembly aptitudes.⁴ Strategies to assemble nanoparticles into complex nanostructures include the polymer-mediated "brick and mortar" approach,⁵ templates,⁶⁻⁹ and the dithiol-mediated nanoparticle aggregation.^{10–13} The last has been utilized to develop novel functional nanomaterials.^{14,15} Yet, spontaneous assembly of nanoparticles, whereby metal nanoparticles self-assemble under certain conditions, is an attractive strategy due to its simplicity. For example, Schaak and co-workers have reported on the spontaneous aggregation of poly(vinylpyrrolidone)-stabilized rhodium nanoparticles into spherical aggregates and superlattices.¹⁶ Cao and co-workers have demonstrated the use of solvophobic interactions to control the formation of Fe₃O₄ superparticles that in turn form near perfect superlattices.¹⁷ The self-assembly between two different types of metal nanoparticles mediated by electrostatic interaction leads to the formation of large diamondlike crystals.¹⁸

Introduction of chromophores into the nanoparticle capping layer may result in systems with novel photophysical properties. For example, gold nanoparticle hybrids with pyrene show very interesting photophysics, including photoinduced charge transfer.^{19–23} Murray and co-workers have studied the dynamic and static fluorescence-quenching processes of five different fluorophores by gold nanoparticles, demonstrating the relationship

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between the particle sizes and the quenching efficiencies.²⁴ Other studies indicate that gold nanoparticles act as very good quenchers for porphyrinic,²⁵ fullerene,²⁶ dansyl,²⁷ fluorenyl,²⁸ perylenediimide,²⁹ and fluorescein³⁰ fluorophores. Importantly, aromatic chromophores can promote self-assembly due to π -stacking and solvophobic interactions. Thus, aromatic dye-capped gold nanoparticles may be very advantageous for creation of photoactive assemblies. An insight into the self-assembly and photonics of such systems would be of fundamental importance for developing new functional nanomaterials and photocatalytic systems.³¹

Perylene diimides (PDIs) represent an important class of aromatic dye molecules. The extended aromatic π -system of the PDI results in strong hydrophobicity, excellent light absorption and luminescence characteristics, and advantageous redox properties,^{32,33} making PDIs useful multifunctional components in self-assembled light-harvesting materials.^{34,35} Molecular systems containing PDI moieties have been reported to aggregate in various solvents due to π - π -stacking and solvophobic interactions.^{29,32-38} We have recently reported on adaptive photofunctional fibers³⁹ and gels⁴⁰ that resulted from the self-assembly of PEG containing derivatives of PDI in aqueous medium.

Herein we report on the spontaneous aggregation of PDIcovered gold nanoparticles into spherical aggregates. The selfassembly is based on solvophobic interactions, allowing control over the size of the assemblies. These systems show complex photophysical behavior, as evidenced by femtosecond transient absorption studies.

Results and Discussion

Perylene diimide (PDI) molecules play a dual role in our strategy: first, they provide a self-assembly motif; second, the PDI chromophores act as light harvesting and redox units that

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may participate in photoinduced electron transfer with the nanoparticles.

The hybrids synthesis was based on the commonly employed ligand-exchange strategy.⁴¹ Accordingly, PDI ligands and gold nanoparticles were chosen to facilitate the ligand-exchange process. We synthesized PDIs bearing a thiol functional group (Scheme 1), which forms very strong bonds with gold nanoparticles,⁴² and gold nanoparticles stabilized by triphenylphosphine (a relatively labile ligand⁴³). The latter system is an excellent precursor for synthesizing a wide variety of nanoparticles by ligand exchange.⁴⁴ Additionally, the gold nanoparticles stabilized by triphenylphosphine are reported to be less than 2 nm in diameter,⁴⁵ of comparable size with the PDI ligand, enabling PDIs to play a pronounced role in the self-assembly process.

The synthesis of the PDI thiol derivatives is outlined in Scheme 1 (see Supporting Information for details). The monosubstituted derivatives were selectively generated by adding 1 equiv of the base to an excess of the dithiol in THF, which then reacted with 1 equiv of the monobromo-PDI, affording the PDI thiols 1 and 2.

The triphenylphosphine-stabilized gold nanoparticles (AuNP) were synthesized following the literature procedure.⁴⁶ The transmission electron microscopy (TEM) analysis of the particles showed an average particle size of 1.5 ± 0.3 nm. The PDIcovered gold nanoparticles 3 and 4 were synthesized by the ligand-exchange reaction between the AuNP and 1 and 2, respectively, carried out at 1:20 (AuNP:PDI) molar ratio in chloroform under inert atmosphere. The progress of the ligand exchange was monitored by steady-state fluorescence over 2 days. A considerable amount of quenching of the PDI fluorescence was observed immediately after the addition of the PDI thiols 1 and 2 to the nanoparticles (Figure 1). The fluorescence of the PDI was quenched by 92% by 1 and 76% by 2, respectively. The quenching is indicative of the formation of the bond between the thiol and the gold nanoparticle. The excess of the ligands was removed by a series of precipitations from hexane followed by centrifugation. ¹H NMR of the resulting precipitate (Figure S5, Supporting Information) revealed a spectrum that shows significant broadening of the PDI protons of 1 and 2, signifying their attachment to the nanoparticle surface.

PDIs are known to stack by $\pi - \pi$ interactions in different solvent environments. This phenomenon had previously been exploited to develop diverse self-assembled structures of different morphologies and sizes.^{32–35,47–51} One of the methodologies uses addition of methanol (an aggregating solvent for PDI) to a solution of PDI in a disaggregating solvent such as chloroform, resulting in aggregation.⁵²

Applying this aggregation methodology to our hybrid systems, we prepared methanol/chloroform solutions of **3**. TEM images of hybrid system **3** (Figure 2a) deposited on a carbon-coated copper grid from a 40% methanol/chloroform solution revealed the formation of well-defined spherical aggregates with an average size of 156 ± 34 nm. The individual gold nanoparticles can be clearly seen arranged in a matrix formed by the organic chromophore (forming the lower contrast region surrounding the nanoparticles). The average interparticle distance in the spherical aggregates of **3** is 3.0 ± 0.8 nm. The images reveal somewhat denser darker regions on the edges of the aggregates, as expected for projections of spherical assemblies.

Further insight into the aggregate structure was gained using scanning electron microscopy (SEM). Representative SEM images of hybrid **3** (Figure 2b,c) confirm the spherical nature of the aggregates. The spheres cluster into large networks, indicating a propensity to secondary aggregation. The aggregate average size is 150 ± 23 nm, in very good agreement with the TEM data. The SEM analysis also provides evidence for the hollow interior of the aggregates. Some of the aggregates that are not fully formed show a mouth-like opening 40-50 nm in size on their surface, revealing a hollow interior typical of vesicles (Figure 2b).

Apart from the spherical aggregates, it was also observed that a small fraction of hybrid 3 (roughly about 5%) aggregates into a regular two-dimensional array (Figure S7, Supporting Information). These little islands of aggregates are also seen around the edges of the three-dimensional structures. They exhibit an average interparticle distance of 3 ± 0.8 nm and may represent the precursors to the three-dimensional aggregate formation. It appears that the nanoparticles arrange in spherical aggregates mainly by the $\pi - \pi$ and solvophobic interactions between the PDIs covering the nanoparticle surfaces. Molecular modeling (see Supporting Information) shows that in a π -stack model between two molecules of 1, having alkyl chains that are completely stretched, the distance between two terminal sulfur atoms that are responsible for AuNP binding is 3.46 nm (Figure S10a, Supporting Information). This model fits well the interparticle distances calculated from the TEM images. The nanoparticle aggregation displays a distribution of interparticle distances (3 \pm 0.8 nm) that could be due to the inhomogeneous particle sizes and conformers of 1. Scheme 2 illustrates the possible assembly pattern of the nanoparticles as a result of the $\pi - \pi$ stacking between PDIs.

Aggregation of the hybrid 3 occurs also when it is deposited from toluene (the latter is known to be an aggregating solvent when multi-PDI systems are involved⁴⁷). Thus, hybrid **3** formed spherical aggregates when deposited from toluene solutions, as shown in Figure 3a. However, these spherical systems are larger and less uniform (average aggregate size of 366 ± 147 nm) than the ones obtained from chloroform/methanol mixtures. Interestingly, the particles exist exclusively as the spherical aggregates, and no free particles or smaller assemblies were observed. The three-dimensional structure of these aggregates is revealed by SEM (Figure 3b), where hybrid 3 shows spherical aggregates with an average size of 436 ± 238 nm. In addition, well-separated aggregates rather than their clusters (as in the case of methanol/chloroform) were observed. This indicates that it is possible to tune the size of nanoparticle aggregates and their secondary aggregation by choice of the solvents from which they are deposited.

It should be noted that when the hybrid particles were deposited from a pure chloroform solution, no formation of spherical aggregates was observed. Only a small fraction of the



Figure 1. Fluorescence quenching of (a) 1 and (b) 2 followed in time after the addition of gold nanoparticles to the PDI-thiol (1:20 molar ratio) in chloroform.





Figure 2. (a) TEM and (b)–(c) SEM images of spherical aggregates of 3 deposited from 40% methanol/chloroform. Insets show images at higher magnification. Individual AuNP can be seen in (c).

entire grid displayed domains (Figure S9, Supporting Information) with less-ordered two-dimensional formations of the nanoparticles. An additional control experiment was done to examine if the precursor gold nanoparticles covered with triphenylphosphine ligand show aggregation behavior. Accordingly, these gold

SCHEME 2: Slice of the Vesicle (Seen in Figure 2)^a



^{*a*} The nanoparticles (brown balls) are assembled on the face of the slice by the $\pi - \pi$ stacking between PDIs (red rectangles; see also Figure S10, Supporting Information). The $\pi - \pi$ stacking is shown only on the front face for the sake of clarity. PDIs are shown only for the stacking pattern.

nanoparticles were deposited from 40% methanol/chloroform solution and were analyzed by TEM. There were no aggregates observed for hybrids **3** and **4**, confirming that the PDI molecules on the surface of the nanoparticles in a solvophobic environment are responsible for the nanosphere formation.

The aggregation behavior of hybrid 4 is similar to that of 3. The TEM images of the samples deposited from 40% methanol/ chloroform solution (Figure 4a) reveal spherical aggregates, 113 \pm 40 nm in diameter. The SEM images (Figure 4b) confirm the spherical nature of these aggregates, which are found to be 107 ± 40 nm in diameter. The average interparticle distance within the aggregates is 2.2 ± 0.5 nm. The aggregation appears to be very effective as almost all of the material existed as spherical aggregates in contrast to 3, which showed a small fraction (ca. 5%) of less-ordered aggregates. Vesicular nature of the aggregates is evident from the SEM, where the hollow interior of the spheres is revealed by several not fully formed spheres (Figure 4b, inset). Molecular models show that in a π -stacked model of two molecules of **2** (Figure S10b, Supporting Information) the distance between the thiol sulfur atoms is 2.47 nm. This distance agrees well with the average interparticle separation, as measured from TEM images.

Hybrid **4**, when deposited from a toluene solution, revealed a very different aggregation picture: dense aggregated networks extending to several hundreds of nanometers in size with no specific shape. TEM also revealed relatively less dense giant networks of the hybrid particles, as shown in Figure S8a (Supporting Information). There were a few spherical aggregates (Figure S8b).

The linker moieties in the PDI-thiols 1 and 2 influence the assembly process. Thus, in chloroform/methanol systems the aggregates of 3 were somewhat larger in average size than those of 4, which appears to be due to the longer linker in the case of 3.

In addition to solid-state assemblies, we studied the solutionphase aggregates of 3 and 4 by dynamic light scattering (DLS). The results are presented in Table 1. The DLS data suggest that the hybrids exist as aggregates in all solvents. The hydrodynamic diameter $(D_{\rm H})$ of hybrid **3** in chloroform was found to be 38 ± 4 nm with a small contribution from aggregates with $D_{\rm H} = 748$ nm. In contrast, **3** and **4** in other solvents exhibited aggregates of much larger sizes. The hydrodynamic diameters $(D_{\rm H})$ of hybrid 3 in 40% MeOH/chloroform and toluene were found to be 192 \pm 20 and 854 \pm 228 nm, respectively, and the $D_{\rm H}$ values for hybrid 4 were found to be 191 \pm 19, 270 \pm 31, and 310 \pm 57 nm, respectively, in chloroform, 40% MeOH/chloroform, and toluene solutions with small contributions from aggregates measuring less than 20 nm. Overall, DLS indicates that polydisperse, relatively large aggregates exist in solution, while further analysis is complicated by the polydisperse nature of the systems and the fact that DLS may overestimate the contribution from large aggregates. Unfortunately, the systems in solution could not be studied by X-ray scattering techniques due to their lack of stability under the experimental conditions.

We note that DLS indicates aggregation in all solvents, while upon drying, TEM and SEM show that ordered spherical structures form only in several cases, most probably due to the interplay of solution-phase self-assembly and drying. Nevertheless, the formation of the spherical structures in the solid state is highly reproducible and insensitive to the aging of the solution from which they are deposited (aging times from 1 h to 3 days result in almost identical systems). Furthermore, control over the assembly size can be achieved by the organic ligand and solvent choice. Thus, although a complex interplay of preaggregation in solution and solvent evaporation is involved in the formation of spherical assemblies, it represents a reliable methodology for creation of spherical gold-PDI nanohybrids. Apparently, van der Waals and solvophobic interactions as well as surface tension are important factors for the formation of hollow spheres in the solid state.

Photophysical Studies

To gain insight into the photophysics of AuNP–PDI hybrids, we performed studies that address the dynamics of the systems following photoexcitation. As mentioned above, we observed quenching of PDI fluorescence in hybrids **3** and **4** in chloroform. Quenching of fluorescence can be explained by energy transfer (including excimer formation), charge separation, or other nonradiative decay pathways competing with the emission. Energy transfer from PDI to other entities is less probable due to the absence of chromophores that have absorption red-shifted from PDI.

In earlier studies, which utilized gold nanoparticles larger than 2 nm and organic chromophores with relatively low oxidation potential, an electron transfer from the organic capping layer to the nanoparticles has been observed.^{19,22,23} In the current study we utilized gold nanoparticles less than 2 nm in diameter, also known as nanoclusters, potentially being able to serve as both electron donors and acceptors.⁵³ The Gibbs free energy change for photoinduced formation of an ion pair (ΔG_{cs}) from two coupled neutral redox components can be estimated using eq 1:^{54,55}

$$\Delta G_{\rm cs} = E_{\rm ox} - E_{\rm red} - E_{\rm s} - \frac{e^2}{\varepsilon_{\rm s} r_{\rm DA}} + e^2 \left(\frac{1}{2r_{\rm D}} + \frac{1}{2r_{\rm A}}\right) \left(\frac{1}{\varepsilon_{\rm S}} - \frac{1}{\varepsilon_{\rm P}}\right)$$
(1)

where E_{ox} and E_{red} are the oxidation potential of the donor and the reduction potential of the acceptor, respectively, E_s is the



Figure 3. (a) TEM and (b) SEM images of spherical aggregates of 3 deposited from toluene. The inset in (a) shows the image at higher magnification.



Figure 4. TEM image (a) and SEM image (b) of spherical aggregates of 4 deposited from 40% methanol/chloroform. The inset shows the image at higher magnification, several hollow spheres are present.

 TABLE 1: Comparison of Shape and Sizes of Aggregates of 3 and 4 in Different Solvents Measured by Electron Microscopy and Dynamic Light Scattering Experiments

			aggregate size (nm		n)	
hybrid	solvent	shape of aggregate	TEM	SEM	DLS $(D_H)^a$	
3 3 3 4	CHCl ₃ 40% MeOH/CHCl ₃ toluene CHCl ₂	random spherical spherical random	156 ± 34 366 ± 147	$\begin{array}{c} 150\pm23\\ 436\pm238 \end{array}$	38 ± 4^{b} 192 ± 20^{b} 854 ± 228 191 ± 19^{b}	
4	40% MeOH/CHCl ₃ toluene	spherical giant network	$113 \pm 40 \\ \gg 100$	$107 \pm 40 \\ \gg 100$	270 ± 31^{b} 310 ± 57^{b}	

^a Hydrodynamic diameter. ^b Denotes the average aggregate size with the major contribution to the scattering intensity.

lowest excited singlet-state energy of the system, e is the charge of the electron, r_{DA} is the ion pair distance, r_D and r_A are the ionic radii, ε_s is the dielectric constant of a particular solvent, and ε_P is the dielectric constant of the solvent in which the electrochemistry was done.

According to the reported studies, gold nanoclusters of size similar to that used for the current study, protected with different aromatic and aliphatic thiols, are oxidized electrochemically at 0.2, 0.5, and 0.7 eV vs SCE (the first, the second, and the third oxidation potentials, respectively).^{30,53,56} The first reduction potential of PDI is -0.65 eV (Figure S20, Supporting Information). The electrostatic barrier and the reorganization energy, the two last terms in eq 1, are almost zero for polar solvents. The total energy available from the absorption of photon by 1 and 2 is about 2 eV. Accordingly, the change in the standard

Gibbs energy for the photoinduced charge separation (ΔG_{cs}) in the PDI–AuNP hybrids in a polar environment are about -1.15, -0.85, and -0.65 eV, respectively (for the first, the second, and the third electron transfer from AuNP to the PDIs in the capping layer). These negative changes in the Gibbs energy imply feasible photoinduced transfer of up to three electrons from the gold nanocluster to the PDI ligands. Conversely, according to the same studies, the same gold nanoclusters can be reduced at -0.15 and -0.4 eV with one and two electrons, respectively. The oxidation potentials of compounds 1 and 2 should be relatively high (above 1.5 eV²⁹), and could not be observed in our electrochemical experiments (Figure S20, Supporting Information). Thus, in polar media the free energy change is negative at least for one electron transfer *from* the PDI covering layer to gold nanocluster ($\Delta G_{cs} \sim -0.4 \text{ eV}$). The



Figure 5. Representative spectra of hybrid 3 in toluene. The sample was excited at 575 nm (\sim 2 mJ cm⁻²).

prediction of the free energy change for the charge separation process occurring in a nonpolar environment is more complicated, and substantially more positive values are expected.^{57,58} This will lower the previously obtained highly negative values of ΔG_{cs} for nanocluster oxidation and will significantly decrease the predicted driving force for the photoinduced nanocluster reduction. Overall, the photoinduced electron transfer in the reported PDI–AuNP hybrids in both directions is theoretically possible and should be sensitive to the polarity of the immediate environment, favoring oxidation of the nanocluster due to more negative ΔG_{cs} .

To follow the electron dynamics resulting from photoexcitation of the hybrids, we carried out preliminary femtosecond transient absorption (fsTA) studies in the visible (vis) and near infrared (NIR) spectral ranges (470-750 and 635-1000 nm, respectively). The NIR spectral range is better suited than the normal visible range (400-700 nm) to follow and identify the evolution of the excited states of PDIs since almost all known species of PDIs in the excited states absorb in this region and have characteristic features there.³⁵ We note that in our NIR experiments an 808 nm notch filter was used to block the fundamental frequency (800 nm) seeding the system, while in the visible region experiments we used a 750 nm short pass filter to block the fundamental. This produced a discontinuity in the measured spectrum in the \sim 745-830 nm region. The experiments were performed on hybrids 3 and 4 in chloroform, chloroform/methanol 60/40 v/v mixture, and toluene. The experimental data were subjected to a global and target fit analysis to obtain the species-associated difference spectra (SADS) and the kinetic components of their evolution.⁵⁹ Illustratively, the SADS obtained from the analysis of the fsTA data for the same samples in different experiments (one in the visible range and another in the NIR using slightly different setup) match spectrally in the overlap region (635-745 nm) of the two experiments and show very similar kinetic time constants, indicating the stability of the experimental system and the consistency of the data analysis methodology. The discontinuity region is marked by gray color in Figures 5, 7, S11, S13, S14, S16, S17, and S19 (Supporting Information). The spectra in this region were interpolated.

Our studies reveal complex photoinduced behavior within **3** and **4**, which is sensitive to the bridging moiety of these hybrid systems. The target fit analysis of the experimental data shows formation of three major photoinduced species. These species have absorption peaks red-shifted from \sim 720 nm, a spectral region characteristic for the absorption features of PDI in the first excited state (S1) and the radical anion of PDI (PDI⁻).³⁵ The overall decay kinetics of **4** were faster than those of **3**,

 TABLE 2: Time Constants of the Kinetic Components of

 SADS Evolution of Hybrid 3 in Different Media Obtained

 Using Target Fit Analysis

hybrid 3	CHCl ₃ /MeOH	CHCl ₃	toluene
$ \begin{aligned} &\tau_1 \ (\text{ps}) \\ &\tau_2 \ (\text{ps}) \\ &\tau_3 \ (\text{ps}) \end{aligned} $	5	6	4.5
	66	54	50
	>2000	>2000	>2000

consistent with the shorter (1 vs 1.6 nm) and partially aromatic nature of the linker coupling the redox components. Unfortunately, hybrid **4** was partially decomposed under the illumination conditions used in these experiments. Therefore, we present only the data analysis regarding hybrid **3** that was stable over time under laser light. The time constants of the kinetic components obtained by target analysis are summarized in Table 2, the representative spectra, representative kinetic traces, and the SADS are shown in Figures 5–7 and S11–S19 (Supporting Information).

To discriminate the S1 appearance from other components contributing to the fsTA signal of 3, a control NIR fsTA experiment on compound 1 was performed in chloroform (Figures S11-S13, Supporting Information). The evolution of the fsTA signal of the free ligand can be described by a combination of two SADS. One $(\tau > 2 \text{ ns})$ with a major contribution (~90%) is a superposition of the S1 positive absorption in the region red-shifted from 700 nm accompanied by the stimulated emission, which appears as a negative signal in the 630–700 nm spectral range. An additional minor (10%) nonradiative decay component ($\tau \sim 100 \text{ ps}$) is contributing to the disappearance of the fsTA signal. This is consistent with the measured fluorescence life time (FLT) (single 8.1 ns component; see Figure S22, Supporting Information). The SADS associated with 100 ps decay component shows a positive absorption at wavelengths greater than 700 nm and lacks the negative (radiative) part.

The target analysis of the evolution of the fsTA signal of hybrid **3** resulted in a satisfactory fit when performed in accordance with the energy level diagram depicted in Scheme 3. The SADS obtained by this analysis (Figure 7) were identified as (1) the first excited state S1 (having characteristic spectral appearance as discussed earlier), (2) an intermediate state spectrally resembling the S1 (designated as IS1; possibly an exciton-like state formed due to the π -stacking of PDIs or a vibrationally relaxed sate), and (3) an additional state not



Figure 6. Decay kinetics of hybrid **3** in toluene pumped at 575 nm (\sim 2 mJ cm⁻²) and probed at the absorption peaks.



Figure 7. SADS (species-associated difference spectra) obtained by global analysis of the transient absorption data for hybrid **3** in toluene. The "short λ experiment" and the "long λ experiment" in the legend refer to the experiments in which the detection was performed in the 450–750 nm and 635–1000 nm ranges, respectively. States corresponding to the energy diagram (Scheme 3): S1, black trace; IS1, red trace; CS, blue trace. The rate constants of the kinetic components associated with the SADS obtained by independent analysis of the experiments acquired at different spectral ranges are mentioned in the legend.

SCHEME 3: Suggested Energy Level Scheme for Hybrid 3^a



^{*a*} The kinetic components found for different samples fall within the presented ranges.

observed for the free ligand (characterized by strong absorption in the 700-750 nm range). On the basis of the steady-state fluorescence measurements and considering the redox potentials of the hybrids' components, the newly formed state 3 appears to represent charge separation (see below). Therefore, we designated this state as charge separated (CS). While theoretically, the light-driven electron transfer can occur in both directions in the PDI-AuNP hybrid (see above), we believe that our measurements point to formation of PDI⁻, indicating electron transfer from AuNP to PDI. Thus, the spectral appearance in the 700-900 nm range (peaking at ~720 nm), characteristic of PDI⁻⁻, the absence of a positive signal in the 550-650 nm range attributed to the PDI⁺,⁶⁰ and the absence of absorption features associated with PDI in the triplet state⁶¹⁻⁶³ support the formation of PDI^{•-.64-68} Chemical reduction of compound 1 using sodium dithionate (Figure S22, Supporting Information) showed the appearance of the 715 nm peak as the main absorption feature of PDI⁻⁻, consistent with our analysis.

To summarize the global fit analysis (Scheme 3 and Figure 7), the S1 state of PDI is created during the pump pulse and decays within a few picoseconds ($\tau \sim 5 \pm 3$ ps), populating the IS1 and the CS states. The IS1 is being converted into the CS within tens of picoseconds ($\tau = 50 \pm 20$ ps); therefore it appears as a superposition of the S1-like state at wavelengths longer than 830 nm and the rising CS signal at wavelengths shorter than 750 nm, where the S1 absorption is relatively low, thus appearing as a negative feature peaking at ~720 nm. Consequently, the CS state converts to the ground state within >2 ns (nonradiatively), a process that can be assigned to a charge

recombination. Slow conversion of S1 into CS through IS1, in comparison with the direct S1 \rightarrow CS transition and the relatively long decay of the CS state, gives rise to a local maximum in the kinetic profiles of hybrid **3** at ~720 nm, ~100-200 ps after the excitation (see Figure 6). We note that our analysis describes the photophysics of the assembly, and therefore all time constants represent averaged values for many different individual hybrids and conformations. Further characterization of the photoinduced electron dynamics in PDI-AuNP hybrids including additional experimental methodologies is currently underway.

The kinetics of the CS-state formation from S1 and from the IS1 state exhibits poor solvent dependence. It may be due to the fact that π -stacking of the PDIs expels the solvent molecules from the vicinity of the aromatic part of PDIs (**3** is aggregated at all solvent conditions), thus decreasing the effect of solvent polarity, whereas the actual permittivity of a medium at short (nanometer) distances from the nanoparticle under excitation can be highly affected by the nanoparticle.¹⁹

In conclusion, hybrid gold nanoparticles covered by perylenediimide ligands (PDI) were synthesized. These hybrids aggregate into spherical nanostructures with a size that can be tuned by the choice of PDI ligand and solvent. Although the photoinduced dynamics in the hybrid self-assembled systems is complicated by the complex structure of the arrays, the polydispersity of the systems, and the difficulty in changing the environment polarity, transient absorption investigation of the hybrids indicates a photoinduced electron transfer from the gold nanoparticles to PDIs. Our study on the hybrids' self-assembly shows that the formation of well-defined nanostructures as well as tuning their sizes can be achieved by employing a combination of the capping ligand choice and regulating the solvophobic interactions between the ligands. This, combined with the photoand redox-active nature of the ligands, demonstrates the possibility to create and optimize functional nanostructures via a simple variation in the ligand linker moiety and the solvent in the systems based on nanoparticle-dye hybrids.

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Supporting Information Available: Experimental details of synthesis and characterization of **1** and **2**, additional electron microscopy images, UV/vis, fluorescence, and NMR spectra, molecular models, transient absorption data, cyclic voltammograms, and emission lifetime measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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