

## MURI 24

# Engineered Multifunctional Nanophotonic Materials for Ultrafast Optical Switching

### CONTRIBUTIONS FOR FINAL REPORTS

#### Marder Research Group

#### **Interactions between Conjugated Ligands and Noble Metals**

Interactions between nonlinear optical organic dyes and assemblies of noble-metal nanostructures may potentially be exploited for optical-switching applications. Our focus has been on studying fundamental aspects of the interactions between conjugated molecules and noble metals.

Au nanoparticles (ca. 3 nm in diameter) coated with bis(diarylamino)biphenyl-based thiols with two different alkyl spacers (propyl and dodecyl) between the chromophore and the surface-anchoring thiol group have been prepared and were characterized (collaboration with **Perry**) with a variety of techniques. The excited-state dynamics of the dyes in close proximity to the nanoparticle surface were studied using the time-correlated single-photon counting technique and near-IR fs transient absorption spectroscopy. The excited states of the dyes in the hybrid metal/organic systems exhibit ultrafast (<5 ps) deactivation, the length of the alkyl spacer between the dye and the thiol group having a profound effect on the ultrafast dynamics. Ultrafast formation (ca. 0.5 ps) of a cation-like species was seen for the propyl system but not for the dodecyl-linker system, and was attributed to dye–dye interactions leading to the formation of a charge-transfer species involving two or more dye molecules.<sup>1</sup>

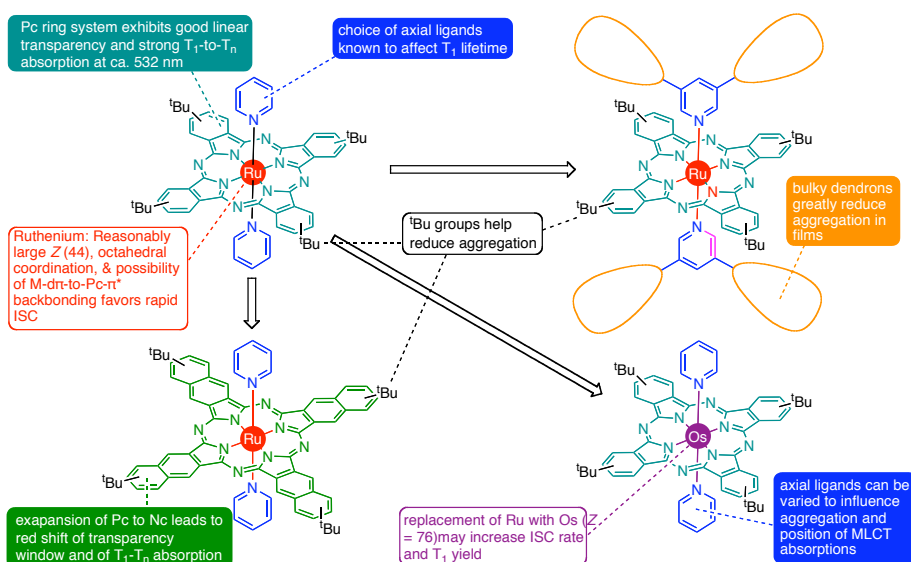
We have also, in collaboration with Antoine Kahn (Princeton) and Georg Heimel (Humboldt, Berlin), investigated the electronic structure of planar Au surfaces coated with variously substituted stilbene thiolates using photoelectron spectroscopy and comparison with theory. In particular, we confirmed for the first time theoretical predictions that  $\pi$ -donors in self-assembled monolayers have only a minor influence on the hole injection barrier from the metal to the organic, despite significantly affecting the molecular ionization potential.<sup>2,3</sup>

We have also supplied thiol ligands to other groups in the program for nonlinear optical measurements.

#### **Heavy-Metal Phthalocyanines with Reduced Aggregation**

Phthalocyanines (Pc) are attractive candidates for optical limiting in the vicinity of 500 nm since they have weak ground-state absorption and strong excited-state triplet absorption at this wavelength. However, it is necessary that the Pc derivative exhibits rapid intersystem crossing and, that the Pcs do not aggregate at high chromophore

densities since aggregation leads to deleterious changes to the absorption characteristics. We investigated several approaches to developing non-aggregating metal-Pcs with high ISC rates by axially coordination of the central metal atom with dendrimeric species. The use of iodine substituents on the dendrimer has relatively minor effects on the triplet yield. Another approach investigated involved appending heavy-metal acetylides to Pc cores, but this also led to limited success. Another, more successful approach involves incorporation of heavy group 8 metals into the Pc (Fig 1), these being attractive due to their preference for 6-fold coordination, allowing for attachment of dendrimers above and below the Pc plane. We have synthesized a range of such species and investigated their optical properties in collaboration with **Hagan, Van Styland, and Perry**. While the spectral peculiarities of RuPc and Nc derivatives, notably the hypsochromic shifts of the Q bands relative to those of, for example, Zn<sup>II</sup> and In<sup>III</sup> analogues, will likely somewhat restrict the wavelength range over which effective OL can be achieved, we have shown the combination of a heavy central atom to promote rapid intersystem crossing and the suppression of solid-state aggregation effects via axially coordinated dendrimers, leads to examples that exhibit strong nonlinear absorption at 475 nm in both solution and neat films.<sup>4</sup>



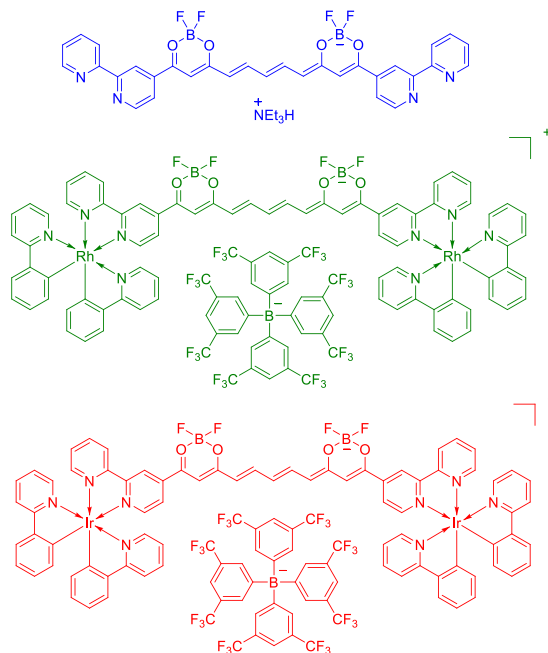
**Figure 1.** General Approach to Ru / Os Pc / Nc derivatives for vis. OL applications.

## Polymethines and Squaraines with Heavy-Metal Functionalization

Polymethines (such as cyanines) exhibit windows of high linear transparency on the high-energy side of their relatively narrow and strong low-energy optical transitions. If strong excited-state absorptions can be obtained at wavelengths corresponding to these windows of near-transparency and if the excited state in question is long-lived, optical pulse suppression based on reverse saturable absorption is feasible at these wavelengths. We have previously found that some polymethines do indeed exhibit excited-state absorptions in this region. Another attractive feature of polymethines is that the absorption maxima, and, therefore, also the windows of transparency, can be varied over a wide range of visible and near-IR wavelengths by varying the chain length and the end groups, allowing development of dyes for the applications at different wavelengths. In

order to achieve long-lived excited states we have been working on incorporating heavy atoms into cyanine-type structures; the strong spin-orbit coupling associated with heavy atoms is hoped to lead to rapid intersystem crossing to afford strong-absorbing long-lived triplet states. We have investigated a number of different synthetic approaches. One such class of metal-functionalized polymethines, studied in collaboration with **Perry** and the **UCF** groups, is shown in Fig. 2. These Rh and Ir-coordinated bipyridine-functionalized bis(dioxaborine) heptamethines open the possibility of postterminal-group metal complexation as a means of modifying the properties of polymethines. Functionalization of this type can also modify the third-order nonlinear optical properties and, at least for the particular counterions used here, potentially mitigate the adverse effects of solid-state aggregation on linear transparency. Metallation results in small increases in the magnitude of  $\text{Re}(\gamma)$  at 1.55  $\mu\text{m}$ , with comparable  $\text{Im}(\gamma)$  associated with 2PA at the same wavelength. In the context of this program, these dyes may be useful for optical pulse suppression based on two-photon absorption.<sup>5</sup>

Squaraines are closely related to polymethines and share a number of spectral characteristics. Accordingly, we have also synthesized a range of new squaraine-based architectures in which multiple squaraines are connected to one another and / or functionalized with heavy-metal acetylides and some of these materials have been studied at **UCF**.

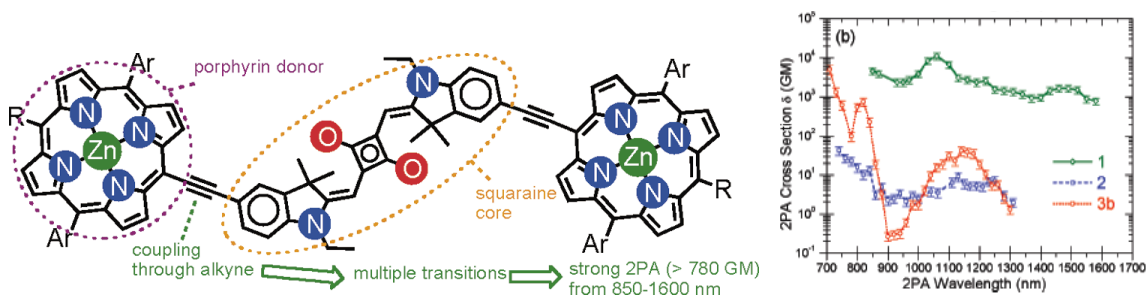


**Fig. 2.** Structure of bis(dioxaborine)-terminated pentamethines functionalized with bipyridine ligands (top) and with Rh and Ir complexes.

## Porphyrin / Squaraine and Porphyrin / Perylene Diimide Triads

Here we investigated (with **Hagan** and **Van Stryland** and with Jean-Luc Brédas at GIT and Harry Anderson at Oxford) the electronic and optical consequences of coupling porphyrin and squaraine or perylene diimide (PDI) moieties in ethynylene-bridged triads. This work was motivated by the observation that squaraines and PDIs have been found to exhibit large 2PA cross-sections at wavelengths close to their one-photon absorption (1PA) edges, while dimers and oligomers of conjugated zinc porphyrins have also been shown to exhibit very strong 2PA, with maximum cross-sections up to 500 times those of monomeric analogues. Moreover, linear absorption spectra of all three classes of compound exhibit bands characterized by large transition dipole moments, a key prerequisite for obtaining strong 2PA. In addition, the S<sub>0</sub>-S<sub>1</sub> transition energies of bis(indolinylidene)methyl squaraines closely match those of porphyrins, suggesting the possibility of substantial excitonic electronic coupling in a  $\pi$ -conjugated hybrid of these two components. On the basis of these observations, we were interested in investigating whether the electronic coupling between the constituent subunits of these triads could be sufficiently strong to result in enhanced 2PA.

The maximum 2PA cross-section of 11 000 GM measured for the porphyrin-squaraine triad (Fig 3) is much larger than that for either model compound but is similar in magnitude to those measured for several other porphyrin dimers with conjugated bridges, for which, however, the maxima are observed at somewhat shorter wavelengths. More unusually, and in contrast to the 2PA spectra of model compounds and other porphyrin dimers, the 2PA absorption of **1** is very broad, with  $\delta > 780$  GM over the entire measurable region, which includes the telecommunications range (1300-1550 nm),<sup>6,7</sup> The enhancement of cross-section suggests substantial electronic coupling between the porphyrin and squaraine moieties; this idea is confirmed by the DFT frontier orbitals. The complexity of this compound and the porphyrin-squaraine coupling are anticipated to lead to a large number of low-lying excited states. Therefore, the broad 2PA spectrum is likely to arise from overlap of several transitions. The calculations support this idea, as they reproduce the main features of the experimental spectrum, indicating peaks with  $\delta \sim 6900$  and  $9700$  GM at transition energies between those of the two strong 1PA states. The observation of large  $\delta$  over a 750 nm-wide wavelength range suggests applications in broadband NIR pulse suppression.



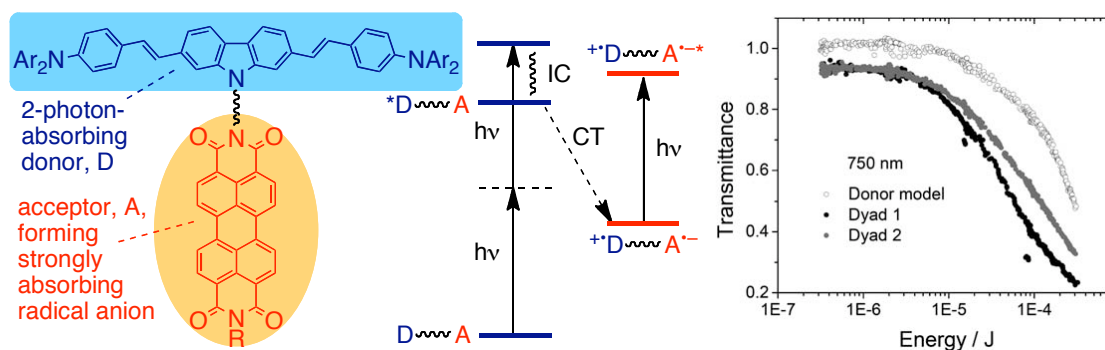
**Figure 3.** Structure of a porphyrin-squaraine triad (left) and 2PA spectra of the triad (**1**) and porphyrin (**2**) and squaraine (**3**) model compounds.

In contrast to that of a related *p*-phenylene-bridged system, the UV-vis-NIR absorption spectrum of the porphyrin-PDI triad deviates significantly from the sum of spectra of isolated porphyrin and PDI units, demonstrating more extensive donor-acceptor

interaction. This finding is consistent with quantum-chemical calculations showing more extensive delocalization of frontier orbitals over both the donor and acceptor, and with electrochemical data. The transient absorption behavior has been investigated in collaboration with M. Wasielewski at Northwestern and is consistent with strong porphyrin-PDI coupling than in the phenylene-bridged analogue. Large 2PA cross sections are found at wavelengths of ca. 1.06-1.20  $\mu\text{m}$ , at which isolated porphyrin and PDI chromophores do not absorb. Quantum-chemical calculations indicate that this 2PA can be attributed to the presence of frontier molecular orbitals with mixed porphyrin and PDI character and that comparably long-wavelength strong 2PA is not expected for the more weakly coupled compound phenyl-bridged analogue.<sup>8</sup>

### Charge-Transfer Optical-Limiting in Donor / Perylene Diimide Assemblies

We have designed and studied systems for optical limiting in which one- or two-photon absorption is followed by formation of strongly absorbing radical ions. We have synthesized and studied two molecular dyads consisting of a 2,7-bis(4-(diarylamino)styryl)carbazole two-photon (2P) absorbing donor, connected by different linkers to a perylene diimide (PDI) acceptor (Figure 4).<sup>9</sup> Photo-induced charge transfer (CT) was characterized using transient absorption measurements. Because of spectral overlap between the donor 2P band and the 1P absorption band of the PDI radical anion the dyads exhibit enhanced nonlinear absorption at 700-800 nm relative to that seen for the 2P donor chromophore. These systems, therefore, represent an example of a 2P charge-transfer approach to optical power limiting. We have also studied related systems based on poly(carbazole-*alt*-fluorene)s with pendant PDI groups. The PDI pendants are aggregated, even in dilute solution, extending the onset of linear PDI absorption into the NIR. Transient-absorption spectra provide evidence for efficient CT following either donor or acceptor photo-excitation to form long-lived charge-separated species, which exhibit strong absorption in the NIR. The spectral overlap between the transient species and the long-wavelength-edge absorption of the aggregated PDI leads to reverse saturable absorption at 680 nm that can be used for optical-pulse suppression. Additionally, at high input energies, 2P mechanisms may also contribute to the suppression. These PDI-grafted polymers exhibit enhanced optical-pulse suppression compared with blends of model materials comprised of unfunctionalized poly(carbazole-*alt*-fluorene)s and PDI small molecules.<sup>10</sup>



**Figure 4.** Schematic for 2PA-induced CT optical limiting in donor-PDI dyads (left) and non-linear transmission behavior in toluene at 750 nm (2 mM, 6 ns pulses, f/5 geometry focussed in center of 1 cm cell) (right). The two dyads differ in the structure of the linker.

1. Malicki, M.; Hales, J. M.; Rumi, M.; Stephen Barlow; McClary, L.; Marder, S. R.; and Perry, J. W., *Phys. Chem. Chem. Phys.* **2010**, *12*, 6267-6277.
2. Malicki, M.; Guan, Z.; Ha, S. D.; Heimel, G.; Barlow, S.; Rumi, M.; Kahn, A.; and Marder, S. R., "Preparation and Characterization of 4'-Donor Substituted Stilbene-4-thiolate Monolayers and Their Influence on the Work Function of Gold", *Langmuir* **2009**, *25*, 7967-7975.
3. Malicki, M.; Heimel, G.; Guan, Z.-L.; Ha, S. D.; Barlow, S.; Kahn, A.; and Marder, S. R., "Energy-Level Alignment in 4'-Substituted Stilbene-4-thiolate Self-Assembled Monolayers on Gold", *J. Phys. Chem. C* **2011**, *115*, 7487-7495.
4. Dasari, R. R.; Sartin, M. M.; Cozzuol, M.; Barlow, S.; Perry, J. W.; and Marder, S. R., "Synthesis and linear and nonlinear absorption properties of dendronised ruthenium(II) phthalocyanine and naphthalocyanine", *Chem. Commun.* **2011**, *47*, 4547-4549.
5. Lin, H.-C.; Kim, H.; Barlow, S.; Hales, J. M.; Perry, J. W.; and Marder, S. R., "Synthesis and linear and nonlinear optical properties of metal-terminated bis(dioxaborine) polymethines", *Chem. Commun.* **2011**, *47*, 782-784.
6. Odom, S. A.; Webster, S.; Padilha, L. A.; Peceli, D.; Hu, H.; Nootz, G.; Chung, S.-J.; Ohira, S.; Matichak, J. D.; Przhonska, O. V.; Kachkovski, A. D.; Barlow, S.; Brédas, J.-L.; Anderson, H. L.; Hagan, D. J.; Stryland, E. W. V.; and Marder, S. R., "Synthesis and Two-Photon Spectrum of a Bis(Porphyrin)-Substituted Squaraine", *J. Am. Chem. Soc.* **2009**, *131*, 7510-7511.
7. Webster, S.; Odom, S. A.; Padilha, L. A.; Przhonska, O. V.; Peceli, D.; Hu, H.; Nootz, G.; Kachkovski, A. D.; Matichak, J.; Barlow, S.; Anderson, H. L.; Marder, S. R.; Hagan, D. J.; and Stryland, E. W. V., "Linear and Nonlinear Spectroscopy of a Porphyrin-Squaraine-Porphyrin Conjugated System", *J. Phys. Chem. B* **2009**, *113*, 14854-14867.
8. Odom, S. A.; Kelley, R. F.; Ohira, S.; Ensley, T. R.; Huang, C.; Padilha, L. A.; Webster, S.; Coropceanu, V.; Barlow, S.; Hagan, D. J.; Van Stryland, E. W.; Brédas, J. L.; Anderson, H. L.; Wasielewski, M. R.; and Marder, S. R., "Photophysical Properties of an Alkyne-Bridged Bis(zinc porphyrin)-Perylene Bis(dicarboximide) Derivative", *J. Phys. Chem. A* **2009**, *113*, 10826-10832.
9. Huang, C.; Sartin, M. M.; Siegel, N.; Cozzuol, M.; Zhang, Y.; Hales, J. M.; Barlow, S.; Perry, J. W.; and Marder, S. R., "Photo-induced charge transfer and nonlinear absorption in dyads composed of a two-photon-absorbing donor and a perylene diimide acceptor", *J. Mater. Chem.* **2011**, *21*, 16119-16128.
10. Huang, C.; Sartin, M. M.; Cozzuol, M.; Siegel, N.; Barlow, S.; Perry, J. W.; and Marder, S. R., "Photoinduced Electron Transfer and Nonlinear Absorption in Poly(carbazole-alt-2,7-fluorene)s Bearing Perylene Diimides as Pendant Acceptors", *J. Phys. Chem. A* *submitted*.