Modular Approach toward Supramolecular Functional Assemblies: Remote Control of Fluorescence

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A supramolecular Zn-porphyrin–free-base porphyrin dyad, in which efficient energy transfer occurs, was constructed. The energy-transfer process can be switched on and off by replacing an axial ligand on the Zn-porphyrin, making it possible to remotely control fluorescence from the free-base porphyrin. An implication to logic gates is discussed.

Processing photons and electrons at the molecular or supramolecular level has received considerable attention in the past decade, which may lay the foundation for the development of molecule-based information processing devices.[1] Electron- and energy-transfer processes provide a means for communication among molecular entities in the device. On–off switching of these processes in response to an external trigger is required to process information. Self-assembly using programmed and selective intermolecular interactions may have advantages over covalent construction in preparing elaborate multicomponent molecule-based circuitry.[2] We previously showed that a noncovalent assembly, which is composed of a light emitting center (Zn-tetraphenylporphyrin; ZnTPP) and a quenching component (4-(phenylazo)pyridine; PhNNPy) connected via kinetically labile but structurally well-defined axial coordination, functions as an electron- and proton-responsive photoswitch.[3] We then showed more recently that an axially coordinated complex of PhNNPy and a covalent dyad of Zn-porphyrin and free-base porphyrin works as a switch for intramolecular energy transfer.[4] As a step forward in line with the development, we wish to report here a completely modular, noncovalent construction of a quencher–donor–acceptor triad and a remote control of fluorescence therein. Modular approach can produce a large library of supramolecules in an economical way, and each module can be independently optimized.[5]

We used the Zn-porphyrin bearing an amidine group (ZnPA) and the free-base porphyrin having a carboxyl moiety (FbPC) to construct a self-assembled donor–acceptor dyad (see Figure 1).[6,7] The amidinium–carboxylate salt bridge is a directional hydrogen-bonding interaction augmented by electrostatic force.[8] Formation of the dyad in toluene/DMSO (99:1) and photophysical processes therein were studied in detail as reported previously.[6] Briefly, the dyad forms with a binding constant of $2.9 \times 10^5\,M^{-1}$ ($M = mol\,dm^{-3}$),[9] in which very fast excited energy transfer from ZnPA to FbPC takes place at a rate of $4.0 \times 10^9\,s^{-1}$ with a quantum yield of 0.89.

A CH_2Cl_2 solution of ZnPA with benzoic acid[10] (20 µM each) exhibits fluorescence in a range of 580–680 nm with a peak at 597 nm, while FbPC shows a large peak at 650 nm and a small one at 712 nm.[11] The latter small peak is diagnostic to the free-base emission, since there is no fluorescence from ZnPA in this region. The intensity of ZnPA fluorescence at 597 nm is decreased to 27% in the presence of the equal amount of FbPC. On the other hand, FbPC-based fluorescence shows a marked increase. Especially, the increase of the 712 nm peak is unequivocal evidence for the sensitization of FbPC fluorescence by ZnPA through energy transfer. None of these behavior pointing to energy transfer was observed when ZnPA was replaced by ZnTPP, indicating that the amidinium–carboxylate interaction is essential for energy transfer to take place and the process is intraensemble.

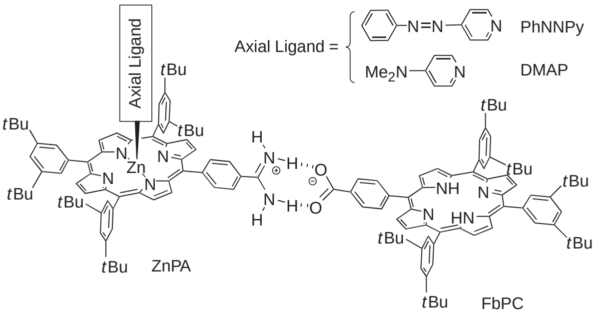

Figure 1. Modular noncovalent assemblies.

While incremental amounts of PhNNPy were added to a 1:1 mixture of ZnPA and FbPC in CH_2Cl_2, the absorption and fluorescence spectra were recorded as shown in Figure 2. The spectral changes, i.e., red shifts by ca. 15 nm of the Q-band peaks of ZnPA, are characteristic to the axial coordination to Zn-porphyrin. Whereas, no detectable change was observed for the absorption by FbPC, see the 647-nm peak. The presence of clear isosbestic points in this change at wavelengths of 555, 580, and 590 nm indicates that a well-defined 1:1 adduct, wherein PhNNPy is coordinating axially to the Zn ion in ZnPA/FbPC, is formed. The association constant (CH_2Cl_2, 25 °C) was determined as $3590 \pm 170\,M^{-1}$ by a non-linear least-squares curve-fitting procedure. PhNNPy quenches Zn-porphyrin fluorescence nearly completely when axially bound.[3,12,13] The quenching of fluorescence from ZnPA is also observed here. More significantly, the fluorescence from FbPC is also quenched even though PhNNPy does not interact directly with FbPC. Thus, PhNNPy suppresses the energy-transfer process from ZnPA to FbPC in the assembly. The residual fluorescence is mainly due to the direct excitation of FbPC.

Then, PhNNPy on the ZnPA unit was replaced by 4-(*N*,*N*-dimethylamino)pyridine (DMAP) simply by adding DMAP to the mixture owing to a stronger association constant of DMAP with ZnPA ($29500 \pm 2400\,M^{-1}$). Further axial coordination is evidenced by the red-shift in the Q-band of ZnPA (Figure 3). A marked increase in fluorescence is observed for the 618 and 651 nm peaks. The 712 nm intensity, which originates purely from the FbPC unit, also increases, even though, again, there is no direct interaction between DMAP and the FbPC unit. These data indicate that (1) the decrease in fluorescence upon the addi-

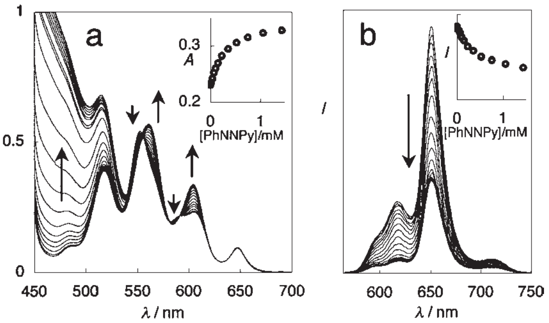

Figure 2. Spectral changes by the addition of PhNNPy (0–2 mM) to a mixture of ZnPA (20 μM) and FbPC (20 μM) in CH_2Cl_2 at 25 °C. (a) Absorption changes. Inset shows absorbances at 604 nm. Absorption by PhNNPy appears at <540 nm. (b) Fluorescence changes ($\lambda_{ex} = 555$ nm). Inset shows fluorescence intensities at 712 nm.

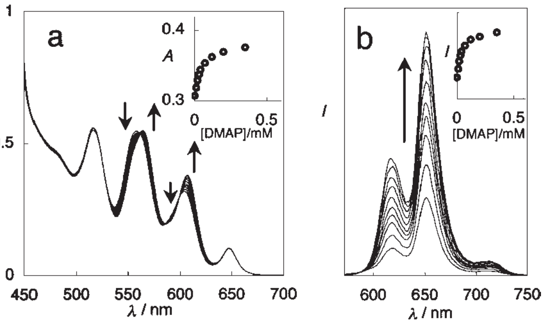

Figure 3. Spectral changes by the addition of DMAP (0–2 mM) to a mixture of ZnPA (20 μM), FbPC (20 μM), and PhNNPy (1 mM) in CH_2Cl_2 at 25 °C. (a) Absorption changes. Inset shows absorbances at 607 nm. (b) Fluorescence changes ($\lambda_{ex} = 561$ nm). Inset shows fluorescence intensities at 712 nm.

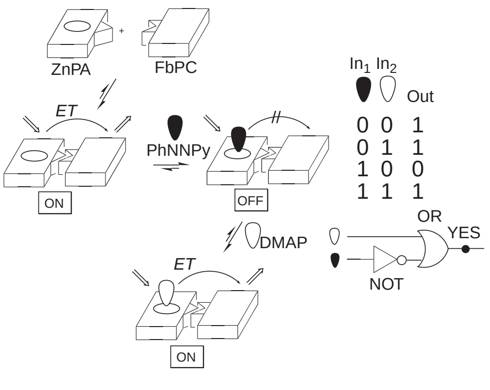

Figure 4. Schematic representation of the remote control of fluorescence. The corresponding logic table and logic diagram are also shown.

tion of PhNNPy is not due to the dissociation of ZnPA and FbPC, and, more importantly, (2) a remote control of fluorescence is possible. The processes explained above are schematically summarized in Figure 4. Repeated on–off switching of the energy-transfer process and resulting fluorescence is a next challenge. In principle, DMAP could be removed or replaced, for example, by using polymer bound materials.

In the meantime, this system can be seen from a point of view of molecular logic gates.[1a–1c] Molecule-based logic gates with optical or chemical inputs/outputs are advantageous, since there is no need to wire individual molecules, which is a challenging issue with no obvious solutions. Taking PhNNPy, DMAP, and fluorescence as Input_1, Input_2, and Output, respectively, the logic table in the present system would be the one shown in Figure 4. The ZnPA unit is an OR gate with one of the inputs (Input_1) inverted through a NOT gate. Then, the FbPC unit is a YES gate that generates the identical output with the input. Thus, energy transfer is used as a means of information transfer at the molecular level.

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9 ZnPA molecules self-associate through axial coordination by the amidine moiety in CH_2Cl_2, making it difficult to analyze the association process. It was confirmed, however, that ≈90% of porphyrins form the desired dyad in a 20 μM solution of ZnPA and FbPC in CH_2Cl_2, based on the absorption and fluorescence titrations. FbPC prevents the self-association of ZnPA molecules by making a stronger amidinium–carboxylate salt bridge.
10 Benzoic acid was used to better model the ZnPA unit in the dyad to prevent the self-association of ZnPA.
11 See Figure S1 in Electronic Supporting Information.
12 PhNNPy used is in the trans isomer. The cis isomer, produced by light irradiation, behaves in the manner identical to the trans isomer in terms of binding and quenching (see Ref. 3).
13 It is possible that the quenching is due to electron transfer from the singlet excited state of ZnPA to PhNNPy, based on energetic considerations (see Refs. 3 and 4), although hard evidence such as transient absorption data has not been obtained.

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