# Anion responsive dyad system of porphyrin and N-confused porphyrin†

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**A dyad of porphyrin and N-confused porphyrin is synthesized for the first time, in which an efficient excitation energy transfer as well as enhancement of emission quantum yield induced by anion binding is observed.**

The study of porphyrin photophysics is of great importance, because such fundamental information is a prerequisite for the development of artificial light harvesting complexes,[1] photosynthetic reaction centers,[2] and molecular devices.[3] As a simple model, a porphyrin dyad system has been often constructed and examined closely.[4,5] Besides, porphyrin dyads bearing switching ability are often investigated to obtain further information on photophysics among porphyrin chromophores.[6] Despite many examples, the switching moiety is usually installed in the bridge part and is hardly ever introduced in the chromophore itself. Herein, a dyad of porphyrin and N-confused porphyrin (NCP)[7] was synthesized for the first time, where the NCP can be used as a switchable chromophore by anion binding.[8] In this dyad system, enhancement of emission quantum yield as well as acceleration of excitation energy transfer was induced by anion binding (Fig. 1).

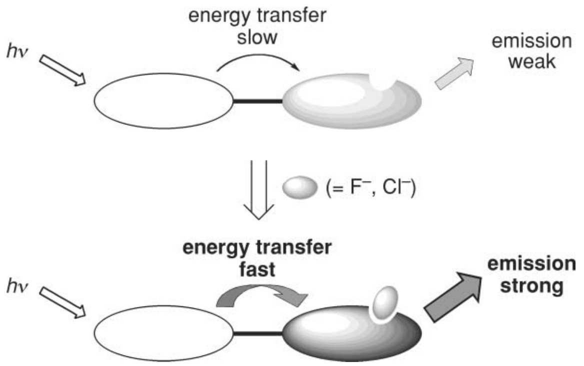

**Fig. 1** Anion responsive dyad system.

Synthesis of the porphyrin–NCP dyad (**1**) was achieved by an acid-catalyzed [2 + 2] condensation reaction of porphyrin-attached normal-type dipyrromethane (**2**) and N-confused dipyrromethane dicarbinol (**3**) as shown in Scheme 1.[9] The pentafluorophenyl groups of the NCP moiety in **1** contribute better yields in dyad synthesis as well as stability against photo-irradiation.[10] The reaction with $CF_3CO_2H$ (16% yield) as an acid-catalyst, so far afforded better yield than the reaction with $CH_3SO_3H$ (8%) or $BF_3{\cdot}OEt_2$ (9%). The structural assignment of **1** is derived from the mass and $^1H$ NMR spectra. In the mass spectrum (MALDI, positive), the parent ion peak is observed at $m/z = 1756.40$ (calcd: 1756.68). The $^1H$ NMR spectrum of **1** in $CDCl_3$ is consistent with the assigned structure. The signals attributable to the outer ($H_a$) and inner ($H_b$) protons of the confused pyrrole moiety are observed at $\delta$ 8.99 and –5.07 ppm, respectively. The signal due to the inner NH protons for the porphyrin moiety is found at $\delta$ –2.54 ppm, while the respective signals for the NCP moiety are at $\delta$ –2.16 and –2.14 ppm. The signals for the *p*-phenylene spacer resonate at $\delta$ 8.57 and 8.69 ppm, and are coupled to each other with $^3J_{HH}$ = 7.9 Hz. The rest of the signals such as the pyrrole β-protons ($\delta$ 8.6–9.3 ppm), the *meso*-aryl protons ($\delta$ 7.8–8.2 ppm), and the protons of the *tert*-butyl groups ($\delta$ 1.55 and 1.58 ppm) can be assigned. 15-Phenyl-5,10,20-tris(pentafluorophenyl) NCP (**4**) was also synthesized in 20% yield by a similar [2 + 2] condensation method as a model compound.

The absorption spectrum of **1** in $CH_2Cl_2$ is shown in Fig. 2 together with the model compounds with the NCP moiety (**4**) and the porphyrin moiety (**5**). The spectrum profile of **1** can be simulated simply by the sum of those of **4** and **5**, suggesting negligible interaction between the two chromophores in the ground state. Hence, the $Q_4$-band (649 nm) originates from the porphyrin moiety and the $Q_5$-band (716 nm) originates from the NCP moiety. This is further supported by theoretical study as discussed below.

The structure of **1** was fully optimized at the B3LYP/6-31G** level and the Kohn–Sham orbitals were analyzed at the same level. The orbital energy levels of the HOMO (0~–3) and the LUMO (0~+3) are summarized in Fig. 3 along with selected Kohn–Sham orbitals. Undoubtedly, orbitals of the porphyrin moiety and the NCP moiety are observed independently. The HOMO and HOMO – 1 are exclusively composed of the porphyrin moiety, while HOMO – 2 and HOMO – 3 are of the NCP moiety. Further, the LUMO and LUMO + 1 are composed of the NCP moiety, while LUMO + 2 and LUMO + 3 are of the porphyrin moiety. As a result, the $Q_5$-band should be derived from the transition from HOMO – 2 to LUMO, while the $Q_4$-band from HOMO to LUMO + 2. The absorption corresponding to the HOMO–LUMO transition is not observed in **1**. Such a clear differentiation of molecular orbitals between the donor and the acceptor would be beneficial for the photophysical study of the dyad system.[11]

Interestingly, addition of $Bu_4N^+F^-$ to **1** in $CH_2Cl_2$ changed the absorption spectrum significantly (Fig. 4a), suggesting the occurrence of anion binding at the peripheral NH group of the NCP as reported previously.[8] Isosbestic points were observed at 446 and 702 nm, indicating a 1:1 binding mode between **1** and $F^-$. $Bu_4N^+F^-$ interacts only with the NCP moiety and negligible interaction with the porphyrin moiety is expected, since almost no

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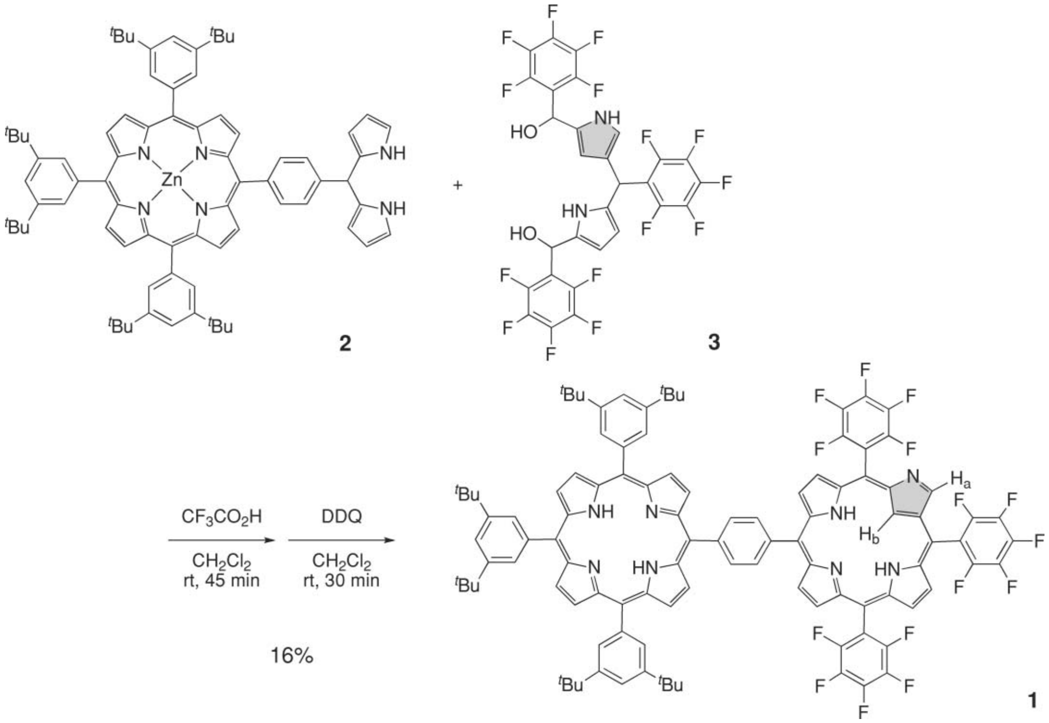

**Scheme 1** Preparation of porphyrin-NCP dyad (**1**).

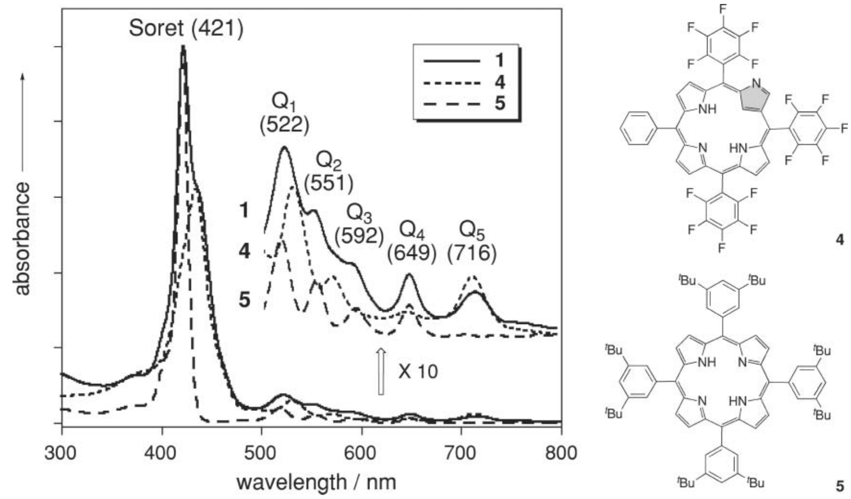

**Fig. 2** Absorption spectra of **1**, **4**, and **5** in $CH_2Cl_2$. The maximum absorption wavelengths are shown in the parentheses.

change was observed in intensity and wavelength of the Soret-band corresponding to the porphyrin moiety at 421 nm. Meanwhile the similar band in the NCP moiety shifted from 434 to 450 nm. Besides, the original $Q_5$-band at 716 nm, which was derived from the NCP moiety, completely disappeared and a new Q-band appeared at 683 nm. This spectral change is consistent with the NH tautomerism induced by anion binding in NCP.[8,12] In contrast, almost no change was observed by the addition of $Bu_4N^+F^-$ to **5** in $CH_2Cl_2$. Thus, the fluoride ion is placed near the peripheral NH moiety and the counter ammonium cation might be placed close to the NCP. This means that the photophysical properties of NCP chromophore can be switched by anion binding even in the dyad system, where a similar trend is not possible by using the porphyrin chromophore. The addition of $Bu_4N^+BPh_4^-$ brought no change in the absorption spectrum, while $Bu_4N^+Cl^-$ afforded a similar result as in the case of $Bu_4N^+F^-$.

To examine the relationship between the excitation energy transfer and the anion binding, the fluorescence spectral change of **1** with increasing amounts of $Bu_4N^+F^-$ was measured (Fig. 4b). A diluted solution of **1** in $CH_2Cl_2$ was excited at 421 nm, where the light was absorbed mainly by the porphyrin moiety. By the addition of $Bu_4N^+F^-$, the emission bands at 730 and 803 nm, which were from the NCP chromophore, shifted to 703 and 765 nm, respectively. The emission intensity directly from the porphyrin chromophore (around 650 nm) was always negligible regardless of the amounts of $Bu_4N^+F^-$ (less than 2% in area ratio) used. This suggested efficient excitation energy transfer from the porphyrin to the NCP chromophore in both cases, before and after the addition

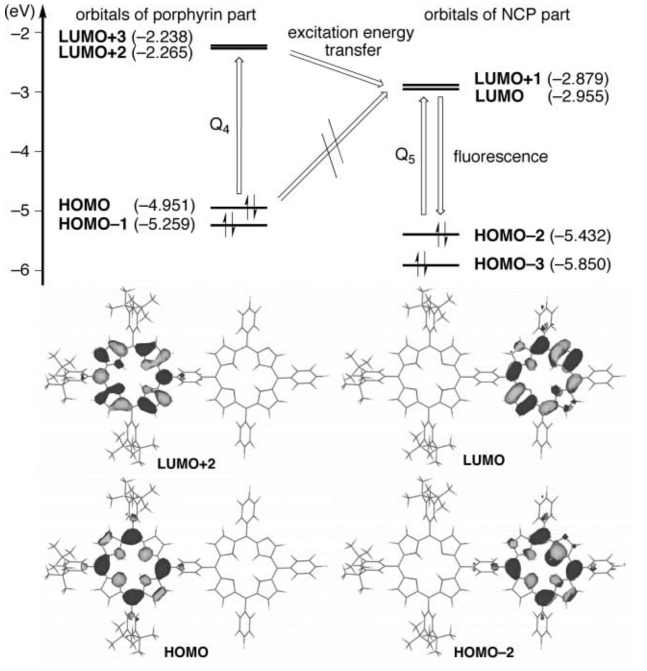

**Fig. 3** Selected orbital energy levels and Kohn–Sham orbitals of **1** calculated at the B3LYP/6-31G** method.

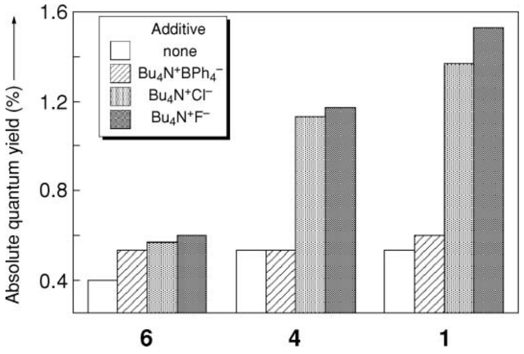

**Fig. 5** Absolute quantum yields of **1**, **4**, and **6** in CH$_2$Cl$_2$.

of Bu$_4$N$^+$F$^-$. The blue shift in the emission spectra (from 730 to 703 nm) was consistent with the blue shift in the absorption spectrum (from 716 to 683 nm) of **1**.

Absolute emission quantum yields ($\Phi_{em}$) of **1**, **4**, and tetrakis(pentafluorophenyl) NCP (**6**) in CH$_2$Cl$_2$ were measured with a calibrated integrating sphere[13] in the presence or absence of excess amounts (~10000 equiv) of ammonium salts (Fig. 5). **4** and **6** were excited at their Soret-bands and **1** was excited at the Soret band of the porphyrin chromophore (421 nm). In **6**, a small enhancement of emission efficiency (from $\Phi_{em} = 0.004$ up to 0.006) was observed with Bu$_4$N$^+$Cl$^-$ or Bu$_4$N$^+$F$^-$. Unexpectedly, the addition of Bu$_4$N$^+$BPh$_4^-$ also gave slightly better emission efficiency although no change was observed in the absorption spectrum. The enhancing effect on emission quantum yields by the added halide anion was remarkable in **4** presumably due to favorable induced dipole moment through anion binding. Similar enhancement of the absolute quantum yields from $\Phi_{em} = 0.0053$ to 0.0153 was observed for **1** in the presence of Bu$_4$N$^+$F$^-$ or Bu$_4$N$^+$Cl$^-$. This means that NCP would be a fascinating chromophore in the dyad system, because its switching ability by anion binding can coexist with excitation energy transfer. Note that essentially the same quantum yields were observed in **1** when the NCP chromophore was directly excited.[14]

Fluorescence lifetime measurements on **1** gave further information on excitation energy transfer from porphyrin to NCP.[15] The porphyrin chromophore was predominantly excited at 420 nm in the lifetime measurements. In the absence of ammonium salt, lifetime of excitation energy transfer was relatively long (40 ps) and emission lifetime was relatively short (370 ps). Expectedly, longer emission lifetimes were observed after the addition of Bu$_4$N$^+$Cl$^-$ (660 ps) or Bu$_4$N$^+$F$^-$ (770 ps) with shorter excitation energy

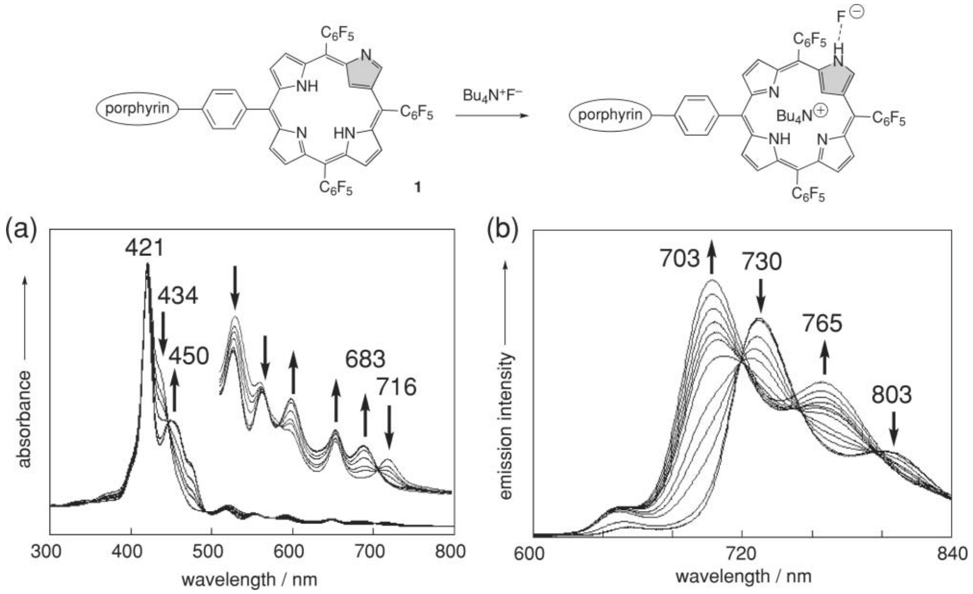

**Fig. 4** Anion binding behavior of **1** in CH$_2$Cl$_2$; (a) absorption spectrum change through addition of Bu$_4$N$^+$F$^-$ (6.6 μM of **1**; 0–18 equivalent of Bu$_4$N$^+$F$^-$), (b) fluorescence spectrum change through addition of Bu$_4$N$^+$F$^-$ (0.69 μM of **1**; 0–32 equivalent of Bu$_4$N$^+$F$^-$; excited at 421 nm).

transfer lifetime (both <10 ps), which was consistent with the better emission quantum yields as described above.[16] Acceleration of energy transfer by anion binding could be explained by increase of a normalized overlap integration factor between absorption of NCP and emission of porphyrin in the Förster equation (see Fig. S5 in ESI).[17]

In conclusion, we have demonstrated the construction of an anion responsive dyad system by connecting a porphyrin and an NCP. When the halogen anion was recognized by the NCP part, the emission quantum yield was significantly improved and the excitation energy transfer became faster. In addition to the anion binding studies, one of the interesting properties of NCP is to generate a wide variety of metal complexes with variable oxidation states and leads to peculiar structures.[18] Some of such complexes possess unique emission properties.[19] Combining a dyad system and the coordination chemistry of NCP would afford interesting molecular devices in the future.

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