Synthesis, excitation energy transfer and singlet oxygen photogeneration of covalently linked N-confused porphyrin–porphyrin and Zn(II) porphyrin dyads

Chun-Ting Poon [a], Shunsheng Zhao [a], Wai-Kwok Wong [a,b,*], Daniel W. J. Kwong [a,*]

[a] Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, PR China
[b] Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong, PR China

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ABSTRACT

Dyads of a N-confused porphyrin (NCP) moiety covalently linked to a porphyrin free-base (H_2P) or a zinc(II) porphyrinate (ZnP) moiety via a flexible alkyl chain of variable length have been synthesized. Photoluminescence study demonstrated an efficient excitation energy transfer from H_2P/ZnP moiety to the NCP moiety. Measurement of the near-IR emission of singlet oxygen produced by these dyads via photosensitization showed that the NCP–ZnP dyads ($\Phi_\Delta = (0.61–0.65) \pm 0.13$) were better $^1O_2$ generators than the NCP–P dyads ($\Phi_\Delta = (0.36–0.41) \pm 0.08$).

Porphyrins have been extensively studied as artificial light-harvesting systems[1] because they absorb light energy strongly, have high fluorescence quantum yield and can act as both donor and acceptor. Numerous systems based on covalently linked multi-porphyrins in the forms of linear and linear-branched arrays,[2] rings,[3] windmills[4] and dendrimers[5] have been developed. Other systems involving porphyrin bridging with another accessory pigment, such as anthracenyl-polyenes,[6] anthracenyl-polyynes,[7] boron-dipyrrin dyes,[8] carotenoids[9] and polyynes,[10] have also been studied. Recently, phthalocyanines, which absorb strongly in the red and green regions, have been linked to porphyrin[11] in order to maximize the capture of the solar energy spectrum because porphyrin, which shows strong absorption in the blue region, absorbs rather weakly in the red and green regions.

N-confused porphyrin (NCP), a structural isomer of porphyrin, was discovered independently by Latos-Grazynski and Furuta in 1994.[12] The structural difference between NCP and porphyrin lies in the inversion of one of the four pyrrole rings, which results in a stronger absorption in the red and green regions as compared to that of the porphyrin.[13] Moreover, NCP can be readily prepared by one-pot synthesis[14] and its peripheral substituents can be easily modified,[15] making it an attractive system to investigate. However, despite the unique photophysical properties of NCP, its excitation energy transfer/electron transfer and photosensitized singlet oxygen generation have not been extensively studied.[16]

To address this important issue, we set forth to synthesize a series of covalently linked N-confused porphyrin–porphyrin dyads in order to examine the excitation energy transfer between these two chromophores. The N-confused tetraphenylporphyrin (NCTPP) was synthesized by Lindsey's method.[14] It was then reacted with an excess amount of dibromoalkane [$Br(CH_2)_nBr$, $n = 3–6$; preparation not successful with $n = 1, 2$] in the presence of Cs_2CO_3 to give the corresponding N-bromoalkylated NCP with isolated yields of ca. 60% (Scheme 1). The target products were obtained by refluxing the N-bromoalkylated NCP with p-OHTPPH$_2$ or Zn[p-OHTPP] in THF in the presence of Cs_2CO_3 in fair yields (ca. 30%) without any difficulty in product separation. The procedures for the preparation of the N-bromoalkylated NCP, NCP–P and NCP–ZnP dyads, together with their characterization data, are given in Supplementary data. Recently, a N-confused porphyrin–porphyrin dyad in which the two moieties were covalently linked through a phenylene bridge have been synthesized and shown to be a good fluorescent anion sensor.[17]

The absorption spectra of the NCP–ZnP and NCP–P dyads, shown in Figure 1, were found to match closely with those observed in the reference system containing a 1:1 molar mixture of ZnP/P and N-methylated N-confused tetraphenylporphyrin (N-Me-NCTPP). The NCP–ZnP dyads (Fig. 1a) exhibit two strong Soret bands at 419 and 450 nm, which correspond to the ZnP and alkylated NCP moieties, respectively. Furthermore, the dyads also display five Q-bands, which correspond to the sum of the Q-bands displayed by the individual moieties. Similar observations were made on the absorption spectra of the NCP–P dyads (Fig. 1b) as well. These results imply that there is no significant electronic

* Corresponding authors.
E-mail address: dkwong@hkbu.edu.hk (D.W.J. Kwong).
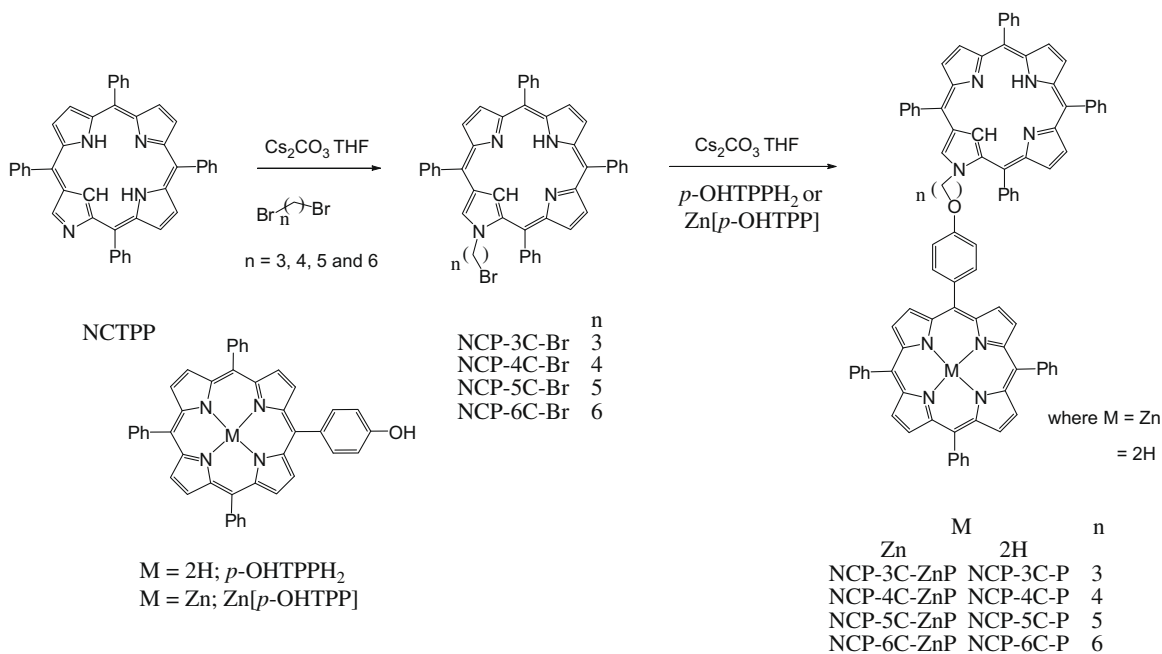
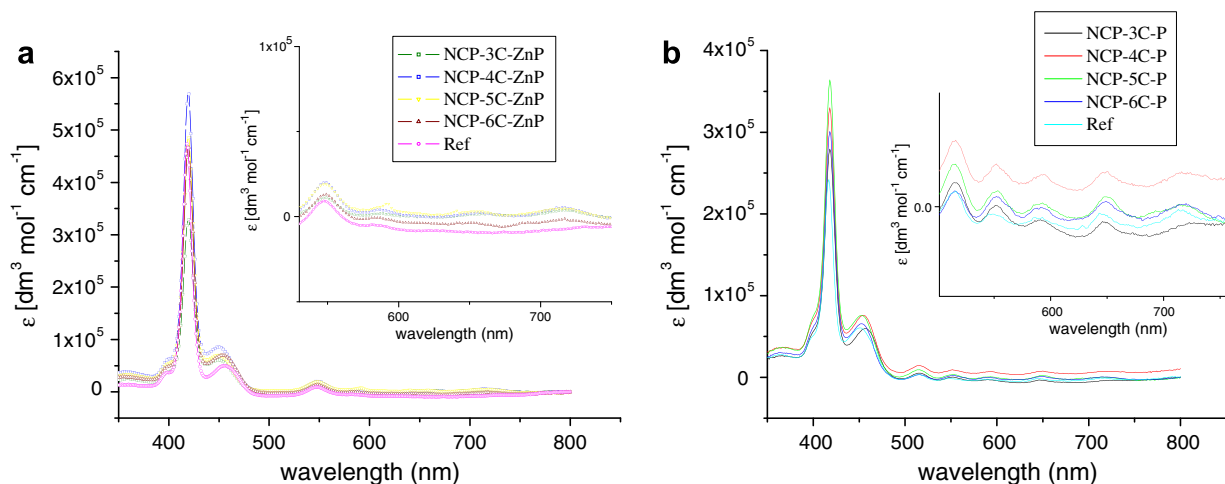**Scheme 1.** Synthetic route of the titled products.

Figure 1. Absorption spectra of (a) NCP–ZnP dyads and (b) NCP–P dyads, compared with the reference system (1:1 molar mixture of N-methylated NCP and ZnP/P), in dichloromethane.

communication between the ground states of the ZnP/P and the NCP moieties.

The emission spectrum of NCP-3C–ZnP (Fig. 2a) obtained by excitation at 421 nm, where ZnP absorbs strongly, shows a weak emission corresponding to the ZnP moiety but a strong emission at 745 nm, which corresponds to the emission of the N-alkylated NCP.[13] When excited at 550 nm, a wavelength absorbed by the ZnP moiety but not by the NCP moiety, the NCP-3C–ZnP dyad exhibited a similar emission spectrum as that excited at 421 nm where the emission from ZnP greatly diminished and the fluorescence of NCP became dominant. As NCP has no/weak absorption at these wavelengths, the emission is apparently due to an excitation energy transfer from the excited state of the ZnP (ZnP*) moiety to the NCP moiety, giving rise to the strong emission observed at 745 nm. The excitation spectrum (from 380 to 730 nm) of this dyad monitored at 745 nm was also found to match closely to its own absorption spectrum (Fig. 2a).

The fluorescence and excitation spectra of the NCP-3C–P dyad were also measured (Fig. 2b). When the dyad was excited at 420 nm, the emission pattern of porphyrin free-base was retained, together with the observation of a broad shoulder at longer wavelengths. Due to the overlapping of the porphyrin and NCP emission, the excitation spectra of NCP-3C–P monitored at different wavelengths were recorded (Fig. 2b). The excitation spectrum, monitored at 655 nm, matched well with the absorption spectrum of porphyrin free-base. But, when monitored either at 728 or 793 nm, the excitation spectrum displayed an additional peak at about 450 nm and resembled the absorption spectrum of the dyad. This indicates that the emissions at 728 and 793 nm were originated from both the porphyrin and the NCP chromophores. Thus, it appears that the energy of the excited porphyrin (P*) is transferred to the NCP moiety. Similar observations were made in dyads with different alkyl chain lengths. The photophysical properties are summarized in Table 1.
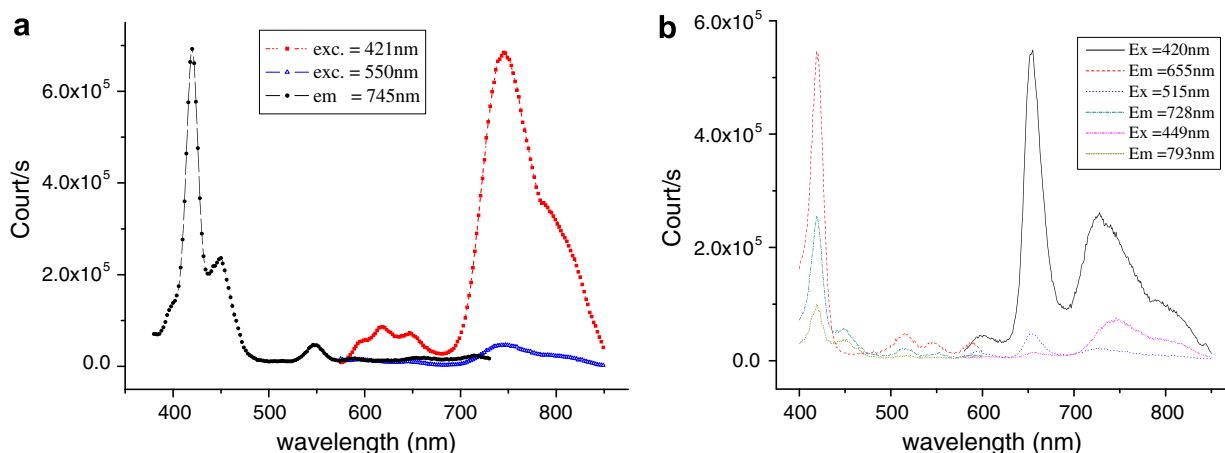
Figure 2. Fluorescence and excitation spectra of (a) NCP-3C–ZnP and (b) NCP-3C–P in dichloromethane.

To determine the nature of the observed excitation energy transfer, that is, radiative versus non-radiative, we examined the overlap of the emission spectrum of ZnP/P with the absorption spectrum of the NCP moiety, shown in Figure S1, as well as the fluorescence decay of the donor (i.e., ZnP and P) in the presence of the acceptor (i.e., NCP).[18] Figure S1 shows significant overlaps of the emission spectra of ZnP and P with the absorption spectrum of the N-Me-NCP. The fluorescence lifetimes of the donors, ZnP and P, were seen to shorten from 1.78 ns and 9.25 ns, respectively,[19] to <0.1 ns[20] and 0.49–0.80 ns when covalently linked with NCP. These observations provide strong support for a non-radiative excitation energy transfer from the ZnP/P* to the NCP moiety in the NCP–ZnP and NCP–P dyads.

The energy transfer efficiency and the energy transfer rate constant between the two moieties of the dyads were also determined. The fluorescence spectra of NCP–ZnP and NCP–P dyads, together with their references of the same concentration, are shown in Figure 3. The fluorescence corresponding to the ZnP/P moiety was highly quenched with concomitant enhancement of the fluorescence of the NCP moiety. This indicates that there is a high degree of energy transfer from the ZnP/P moiety to the NCP moiety when they are covalently linked via a flexible alkyl chain.

The calculated results are summarized in Table 1. The energy transfer efficiency and the rate of energy transfer of NCP–ZnP dyads, determined by steady-state method,[21] ranges from 87.8% to 94.4% and $3.92 \times 10^9 \, s^{-1}$ to $8.96 \times 10^9 \, s^{-1}$, respectively. These results imply nearly quantitative energy transfer in this system.

On the other hand, as the emission of the NCP and P moiety overlaps with each others, time-resolved method[22] was used to determine the energy transfer efficiency and the rate of energy transfer of the NCP–P dyads. The efficiency and rate of energy transfer could be as high as 94.8% and $1.93 \times 10^9 \, s^{-1}$, respectively. Moreover, the distance-dependence of the transfer process was studied and shown to be in line with the prediction from Förster transfer mechanism,[23] with the exception that the energy transfer efficiency for $n = 5$ was lower than that of $n = 6$. This observation can be explained by a possible folding back of the two chromophores via the longer and flexible six-carbon alkyl chain, making them spatially closer for energy transfer in the $n = 6$ dyads. Similar phenomenon has been reported in the bisporphyrin system.[24]

When an aerated chloroform solution of the dyads was photo-irradiated, a NIR emission centered at 1270 nm, corresponding to the phosphorescence of the singlet oxygen ($^1O_2$), was observed (Figs. S2 and S3). The $^1O_2$ yields of the dyads, together with their reference systems, that is, the 1:1 mixture of N-Me-NCP with P/ZnP, were determined by measuring their NIR emission intensities (i.e., peak areas) upon photo-irradiation relative to that of H_2TPP, which shows a $^1O_2$ quantum yield Φ_Δ of 0.55. The results, which are summarized in Table 2, show that the $^1O_2$ yields of the dyads depend on the photo-excitation wavelength. When photo-excited at 421 nm, a wavelength corresponding to the Soret absorption band of the porphyrin moiety, the relative $^1O_2$ quantum yields of the NCP–P dyads ($\Phi_\Delta = (0.36$–$0.41) \pm 0.08$) are significantly lower than that of the 1:1 mixture of H_2TPP and N-Me-NCP reference ($\Phi_\Delta = 0.53 \pm 0.11$). This result shows that a significant amount of the photo-excitation energy absorbed by the TPP moiety is transferred to the NCP moiety, resulting in a smaller amount of excitation energy available for the production of $^1O_2$ via intersystem crossing. When photo-excited at 460 nm, a wavelength corresponding to the Soret absorption of the NCP moiety, the relative $^1O_2$ yields of the NCP–P dyads ($\Phi_\Delta = (0.23$–$0.27) \pm 0.05$) are also significantly lower than that of the 1:1 mixture of H_2TPP and N-Me-NCP reference ($\Phi_\Delta = 0.32 \pm 0.06$) as well as the N-Me-NCP ($\Phi_\Delta = 0.33 \pm 0.06$). Since the NCP–P dyads have much higher vibrational degrees of freedom than the N-Me-NCP, it is reasonable to suggest that a substantial amount of the NCP Soret excitation energy in the NCP–P dyads was dissipated by intramolecular vibrational relaxation, resulting in the lower $^1O_2$ yields observed. This notion is consistent with the observation of a lower fluorescence quantum yield for N-Me-NCP as compared to that of NCTPP where this was interpreted as the presence of the N-methyl group providing a mechanism for deactivation via an increase in the internal conversion rate constant.[13]

Table 1
Photophysical properties, including energy transfer efficiency (Φ_{ET}) and energy transfer rate constant (k_{ET}), of ZnTPP–NCP and TPP–NCP dyads

	Φ_F		$\tau_{F \, (Donor)}$, ns	Φ_{ET}, %	k_{ET}, ns^{-1}
	$\Phi_{F \, (total)}$	$\Phi_{F \, (Donor)}$			
ZnTPP-3C-NCP	0.00648[a]	0.00147[a]	nd[c]	94.4[e]	8.96[e]
ZnTPP-4C-NCP	0.00470[a]	0.00155[a]	nd[c]	94.0[e]	8.50[e]
ZnTPP-5C-NCP	0.00517[a]	0.00313[a]	nd[c]	87.8[e]	3.92[e]
ZnTPP-6C-NCP	0.00471[a]	0.00302[a]	nd[c]	88.2[e]	4.08[e]
TPP-3C-NCP	0.01800[b]	nd[c]	0.492[d]	94.8[f]	1.93[f]
TPP-4C-NCP	0.00910[b]	nd[c]	0.504[d]	94.6[f]	1.88[f]
TPP-5C-NCP	0.02030[b]	nd[c]	0.803[d]	91.5[f]	1.34[f]
TPP-6C-NCP	0.04510[b]	nd[c]	0.603[d]	93.6[f]	1.55[f]

[a] ZnTPP ($\Phi_F = 0.03$ in benzene)[25] as reference.
[b] H_2TPP ($\Phi_F = 0.11$ in benzene)[25] as reference.
[c] Non-detectable.
[d] Measured at 605 nm.
[e] Determined by steady-state method.
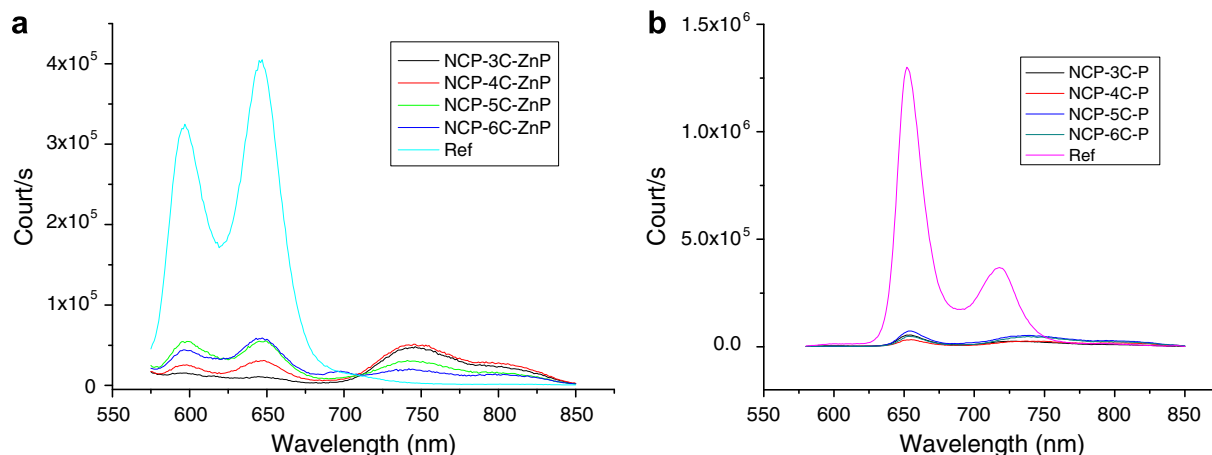[f] Determined by time-resolved method.

a

b

Figure 3. Fluorescence spectra of (a) NCP–ZnP dyads and (b) NCP–P dyads, compared with their reference systems (a 1:1 molar mixture of N-methylated NCP and ZnP/P), in dichloromethane.

Table 2
Relative singlet oxygen quantum yields of NCP–P and NCP–ZnP dyads measured in chloroform using H_2TPP as reference[a]

Compound	Singlet oxygen quantum yield, Φ_Δ,[b]	
	λ_{ex} = 421 nm	λ_{ex} = 460 nm
NCTPP		0.23
N-Me-NCTPP		0.33
H_2TPP + N-Me-NCTPP (1:1)	0.53	0.32
TPP-3C–NCP	0.38	0.23
TPP-4C–NCP	0.36	0.27
TPP-5C–NCP	0.41	0.25
TPP-6C–NCP	0.40	0.25
ZnTPP + N-Me-NCTPP (1:1)	0.56	0.31
ZnTPP-3C–NCP	0.63	0.32
ZnTPP-4C–NCP	0.65	0.31
ZnTPP-5C–NCP	0.61	0.34
ZnTPP-6C–NCP	0.61	0.32

[a] Singlet oxygen quantum yield of H_2TPP, $\Phi_\Delta = 0.55 \pm 0.11$.
[b] Singlet oxygen quantum yields of the dyads were determined by measuring the peak areas of the NIR emission of $^1O_2$ centered at 1270 nm generated by these compounds and compared to that generated from the reference standard H_2TPP upon photo-excitation. The measurement uncertainties were ca. ±20%.

When photo-excited at 421 nm, a wavelength corresponding to the Soret excitation of the ZnP moiety, the $^1O_2$ yields of the NCP–ZnP series ($\Phi_\Delta = (0.61–0.65) \pm 0.13$) appear to be higher than that of the 1:1 mixture of ZnTPP and N-Me-NCP reference ($\Phi_\Delta = 0.56 \pm 0.11$). But, due to the relatively large uncertainty associated with these data, it is not clear whether there is any significant difference in $^1O_2$ yield between the NCP–ZnP dyads and their reference. However, the observation that the $^1O_2$ yields of the NCP–ZnP dyads (average $\Phi_\Delta = 0.63 \pm 0.13$) are higher than those of the NCP–P dyads (average $\Phi_\Delta = 0.39 \pm 0.08$) is reliable and has been attributed to the higher triplet quantum yield of ZnP ($\Phi_T = 0.86 \pm 0.17$) relative to that of H_2TPP ($\Phi_T = 0.73 \pm 0.10$).[26] When photo-excited at 460 nm, which corresponds to the Soret absorption of the NCP moiety in the NCP–ZnP dyads, no discernible difference in $^1O_2$ yield was observed between the dyads ($\Phi_\Delta = (0.31–0.34) \pm 0.06$) and their reference ($\Phi_\Delta = 0.31 \pm 0.06$). Apparently, the photosensitized production of $^1O_2$ at 460 nm occurs principally at the NCP chromophore in the NCP–ZnP dyads.

In conclusion, a series of dyads, in which a N-confused porphyrin (NCP) moiety was covalently linked to a porphyrin free-base (H_2P) or zinc(II) porphyrinate (ZnP) moiety via a flexible alkyl chain of variable length, have been synthesized. A rational design of the synthetic scheme has been developed, which can be widely used in various functionalization of NCP. Photoluminescence studies show that energy is transferred from the excited state of the porphyrin free-base or Zn(II) porphyrin to the NCP moiety, with most of donor fluorescence being quenched (ca. 90%). NIR luminescence measurement shows that the NCP–ZnP dyads are better $^1O_2$ generators than the free porphyrin, H_2TPP, and the NCP–P dyads. This present work demonstrated that the NCP moiety is a good potential candidate for artificial light-harvesting.

Acknowledgements

Supplementary data

Supplementary data (the general procedures for the preparation of the N-bromoalkylated NCP, NCP–P and NCP–ZnP dyads, together with their characterization data, are given in the supplementary content. The spectral overlaps of the emission spectra of H_2TPP and ZnTPP with the absorption spectrum of N-methyl-N-confused tetraphenylporphyrin (N-Me-NCTPP) and the near-IR phosphorescence spectra of the singlet-oxygen generated from TPP-C_n–NCP and ZnTPP-C_n–NCP dyads (n = 3–6) upon photo-excitation) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.11.101.

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20. Due to the limitation (time resolution $\geqslant 0.1$ ns) of our instrument, the exact fluorescence lifetimes of the ZnP chromophore in the NCP–ZnP dyads could not be determined.

21. For the steady-state method, the energy transfer efficiency (Φ_{ET}) and energy transfer rate constant (k_{ET}) can be calculated by the following equations:

$$\Phi_{ET} = (1 - \Phi_D / \Phi_D^o) \times 100\%$$

$$k_{ET} = (1/\Phi_D - 1/\Phi_D^o) \times (\Phi_D^o / \tau^o),$$

where Φ_D is the quantum yield of donor with acceptor, Φ_D^o and τ^o are the quantum yield of donor and lifetime without acceptor, respectively. Faure, S.; Stern, C.; Guilard, R.; Harvey, P. D. J. Am. Chem. Soc. **2004**, 126, 1253.

22. For the time-resolved method, the energy transfer efficiency (Φ_{ET}) and energy transfer rate constant (k_{ET}) were calculated by the following equations:

$$\Phi_{ET} = (1 - \tau_D / \tau_D^o) \times 100\%$$

$$k_{ET} = (1/\tau_D - 1/\tau_D^o),$$

where τ_D is the lifetime of the donor with the acceptor, τ_D^o is the lifetime of the donor without the acceptor present. For further details, please see Ref. 8.

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