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ORIGINAL PAPER

Fluorescence Properties of Phenol-Modified Zinc Phthalocyanine that Tuned by Photoinduced Intra-Molecular Electron Transfer and pH Values

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Abstract Tetra[α-(4-hydroxyphenoxy)] zinc phthalocyanine, ZnPc(α-OPhOH)$_4$, was synthesized and its photophysics was found to be sharply pH dependent. Dual fluorescence emission around 700 nm was observed when it is dissolved in basic solution. The fluorescence of the phthalocyanine can be sharply switched off at pH 9.1 due to the intramolecular photoinduced electron transfer (PET) in ZnPc(α-OPhONa)$_4$, formed by the deprotonation of ZnPc(α-OPhOH)$_4$. The photophysics of both ZnPc(α-OPhOH)$_4$ and ZnPc(α-OPhONa)$_4$ were studied in detail by UV-vis absorption, steady state and time-resolved fluorescence and transient absorption (TA) to reveal the fluorescence quenching mechanism. Intra-molecular PET in ZnPc(α-OPhONa)$_4$ from the donor, PhONa subunits, to the acceptor, ZnPc moiety, was characterized by the much smaller fluorescence quantum yield (0.003) and lifetime (<0.20 ns). PET was further evidenced by the occurrence of charge separation state (CSS) in TA spectra, i.e. the bands due to anion radical of ZnPc and phenol radical. The lifetime of the charge separation state is ca. 3 ns, the efficiency of PET is ca. 99% and the rate constant of PET is 2.3×10^{10} s^{-1}.

Keywords Phthalocyanine · Fluorescence · Fluorescent probe · Photoinduced electron transfer

Introduction

Phthalocyanines (Pcs), with structures as shown in Scheme 1, have gained widespread applications in diverse areas [1–4], such as chemical sensors to hydrogen peroxide and NO$_2$ etc [5–8], due to the excellent physical and chemical properties, as well as their thermal and photo stabilities. Pcs have the potential as PET (photoinduced electron transfer) based fluorescent probes owning to the following advantages: 1) their fluorescence emission is in the red region which is remarkably longer than the auto fluorescence that interferes with the measurement, 2) their adaptability is well known since the wavelength absorption and other properties can be tuned by easy structural modification or through substitution of metal centers, 3) they are biocompatible which have been shown by many tests during the study of photodynamic therapy of tumor, 4) Pcs are good electron acceptors or donors for PET as we have shown in previous reports [9–14]. Fluorescein and its derivatives, the most popular probes [15–17], however, are almost exclusively sensitive to acidic or near neutral pH values.

Phenolate is a proton acceptor due to the equilibrium: PhOH ⇆ PhO$^-$ + H$^+$, the pK$_a$ of this reaction is close to 9.5 and therefore suitable for the measurement of basic pH values. In this study, we synthesize the phenol modified ZnPc, measure the dependence of fluorescence on the pH values, and elucidate the mechanism of the dependency, which is revealed to be PET from phenolate to ZnPc.

Materials and Methods

Reagents and Apparatus

All reagents for synthesis were analytical grade and used as received. ^{1}H NMR spectra were recorded at room temperature on a Bruker dmx 300 MHz NMR spectrometer. MS spectra were recorded either on a Bruker APEX II or

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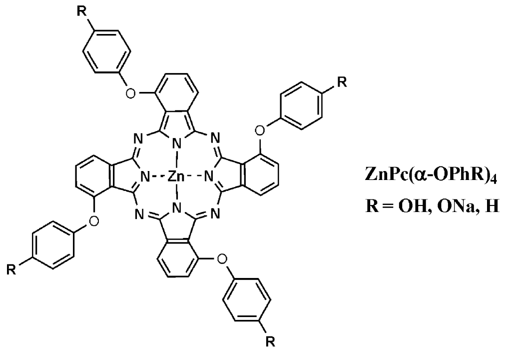

Scheme 1 Chemical structures of adopted phthalocyanines

Autoflex III Maldi-TOF spectrometer. IR spectra were recorded at room temperature on a Shimadzu FTIR-8900 spectrometer. UV-visible spectra were recorded on a Shimadzu 4500 spectrophotometer using 1 cm matched quartz cuvettes.

Synthesis of 3-(4-hydroxyphenoxy)phthalonitrile

5.19 g (0.03 mol) 3-nitrophthalonitrile and 16.5 g (0.15 mol) hydroquinone were added to 30 ml DMF, the resulted solution was heated at 80°C under nitrogen for 6 h, during which 20.7 g (0.15 mol) anhydrous potassium carbonate was added. After cooling down, the product solution was added to 500 ml ice-water to precipitate and filter, the obtained solid was washed with dilute acetic acid to pH 6.0 and dried under vacuum. 3.3 g slight yellow solid was obtained after recrystallization with absolute ethanol. Yield 47%. m.p. 178–179°C. IR(KBr),ν(cm^{-1}): 3402 (Ar-OH), 2236 (CN), 3029 (Ar-H), 1585 (Ar), 1508 (Ar), 1467 (Ar), 1445 (Ar), 1310, 1255, 1197, 1096, 1075, 982, 809, 791. ^{1}H NMR (DMSO-d_6, ppm): δ9.615 (s, 1H), 7.761–7.718 (t, 2H), 7.138–7.071 (q, 1H), 7.071–7.009 (d, 2H), 6.858–6.785 (d, 2H). MS, m/z: 237.3 $[M+H]^+$.

Synthesis of tetra[α-(4-hydroxyphenoxy)] Zinc Phthalocyanine, ZnPc(α-OPhOH)$_4$

In 5 ml *n*-pentanol, 30 mg (4.25 mmol) lithium was added under N_2 and heated for several minutes until it completely dissolved. 47 mg (0.21 mmol) zinc acetate, and 200 mg (0.85 mmol) 3-(p-hydroxylphenoxy)phthalonitrile were then added and heated at 135°C for 1 h. after cooling down, the resulted solution was poured into 200 ml methanol containing 1 M HCl. Methanol was removed by rotavapor under reduced pressure and the remaining solution was treated with chloroform to obtain green solid product. After filtration and washing with chloroform, acetonitrile and water, the solid was purified by column chromatography with THF-ethanol as eluent, 64 mg dried product was obtained, yield 30%. IR (KBr), ν (cm^{-1}): 3419 (Ar-OH), 3029 (Ar-H), 1636 (Ar), 1506 (Ar), 1477 (Ar), 1450 (Ar), 1331, 1233, 1194, 1125, 1091, 744. ^{1}H NMR (DMSO-d_6, ppm): δ 9.322 (s, 1H), 8.863–8.796 (d, 1H), 8.089–8.017 (t, 1H), 7.605–7.502 (d, 1H), 7.408–7.292 (d, 2H), 6.968–6.718 (d, 2H). MS, m/z: 1010.7 $[M+H]^+$.

Photophysics

The absorption and fluorescence spectra, fluorescence quantum yields and excited singlet-state lifetimes, as well as triplet properties were investigated at room temperature. Steady-state fluorescence spectra were acquired on a FLS 920 with 1 nm slit width for both excitation and emission monochromators. All spectra were corrected for the sensitivity of the photo-multiplier tube. The fluorescence quantum yield (Φ_f) was calculated by $\rightleftarrows \Phi_f = F_sA_0\Phi^0{}_f/(F_0A_s)$, in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, the subscript 0 stands for a reference compound and s represents samples. Zinc phthalocyanine was used as the reference ($\Phi_f{}^0 = 0.30$) [18]. Excitation wavelengths of 615 nm corresponding to S_0 to S_1 transitions were employed. The sample and reference solutions were prepared with the same absorbance (A_i) at the excitation wavelength (near 0.09 per cm). All solutions were air saturated.

Fluorescence lifetime of S_1 was measured by time-correlated single photon counting method (Edinburgh FLS920 spectrophotometer) with excitation at 672 nm diode laser (50 ps FWHM) and emission was monitored at 710 nm.

Transient Absorption spectra were recorded in degassed methanol (prepared by bubbling with Argon for 20 min) with an Edinburgh LP920 laser flash photolysis system. A Nd:YAG laser (Brio, 355 nm and 5 ns FWHM) was used as excitation source. The analyzing light was from a xenon lamp. The laser and analyzing light beams perpendicularly passed through a quartz cell with an optical path length of 1 cm. The signal was displayed and recorded on a Tektronix TDS 3012B oscilloscope and an Edinburgh LP920-R928B detector. The laser energy incident at the sample was attenuated to a few mJ per pulse. Time profiles at a series of wavelengths from which point by-point spectra were assembled were recorded with the aid of a Pc controlled kinetic absorption spectrometer. The concentrations of the target compounds were typically 10 μM providing A_{355}=0.25 in a 10 mm cuvette.

Results and Discussion

Figure 1 shows the dependence of the fluorescence of ZnPc (α-OPhOH)$_4$ on pH values. The spectra were measured by excitation at 615 nm and the concentration of ZnPc(α-OPh-

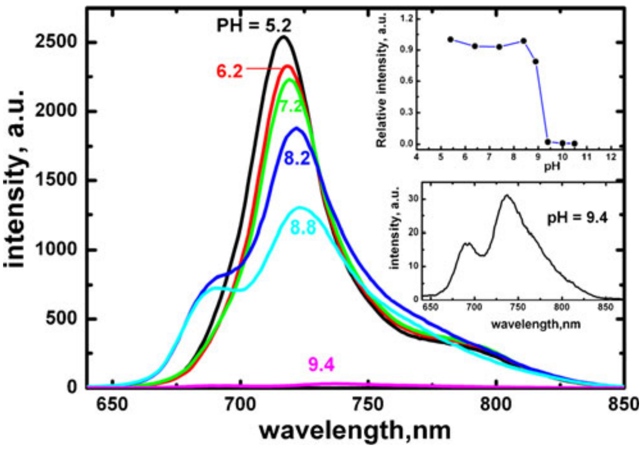

Fig. 1 The fluorescence spectra of ZnPc(α-OPhOH)$_4$ at different pH values, which were measured by excitation at 615 nm in 4.0 mM NaH_2PO_4-Na_2HPO_4 water-DMSO (1:1.5 v/v) buffer. The concentration of ZnPc(α-OPhOH)$_4$ was kept constant at 10 μM. The pH value was adjusted by changing the ratio of NaH_2PO_4 to Na_2HPO_4. The inset top is the plot of fluorescence integrated intensity against pH values. The inset bottom is the amplified view of the emission spectrum at pH 9.4

OH)$_4$ at each pH was kept constant. The corresponding UV-vis absorption spectra were displayed in Fig. 2. Due to the easy formation of H-aggregate in pure water buffer, Water-DMSO (1:1.5 v/v) buffer was employed as the solvent.

The decrease of emission intensity occurred upon the increase of pH, accompanied by the red shift of fluorescence maximum. In addition, an abrupt drop was observed at pH ~9.2 (inset top), close to the pK$_a$ of phenol. At pH 9.4 more than 98% fluorescence was quenched. At this pH, phenol moiety is almost completely dissociated to phenolate, which is responsible for the efficient quenching of the fluorescence of ZnPc moiety. The negative charged phenolate is a much better electron donor than its conjugate acid, which facilitates intramolecular PET. The isosbestic points were observed in the absorption spectra (Fig. 2), suggesting that the dissociation equilibrium holds for pH range from 6.4 to 8.9. At pH 9.4, however, the spectrum deviated from the isosbestic points, indicating that only phenolate exists under the condition. The absorption maxima were also gradually shifted to longer wavelengths with the increase of pH, matching the observations in the emission spectra. This red shift is apparently due to the stronger electron-donating effect of PhO^- than that of PhOH on ZnPc π-system.

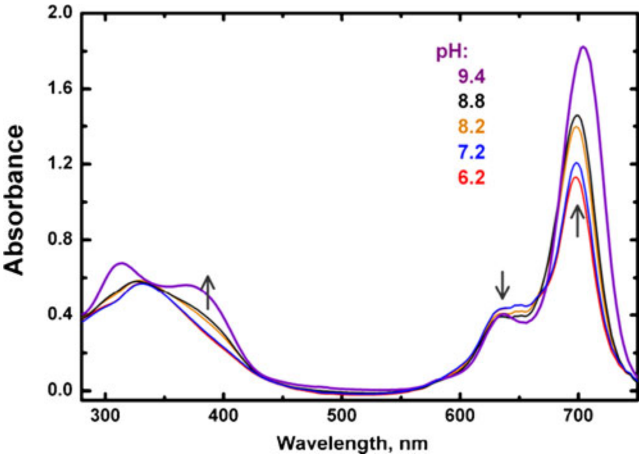

Fig. 2 The UV-vis spectra of ZnPc(α-OPhOH)$_4$ at different pH values in 4.0 mM NaH_2PO_4-Na_2HPO_4 water-DMSO (1:1.5 v/v) buffer. The concentration of ZnPc(α-OPhOH)$_4$ was kept constant at 6 μM

One additional emission band around 685 nm showed up (Fig. 1 and its inset) when pH reached the values such that the solution is sufficiently basic and PhO^- was formed, this suggests that a new emitting species was generated in these cases and it exists only in basic solution, so the deprotonated ZnPc−O−PhO^-Na^+ is the fluorophore responsible for the weak emission. The dual emissive nature of the fluorescence permits that the pH measurement can be carried out based on the intensity ratio of two emission bands. This single excitation-dual emission is highly desirable for an ideal probe since this overcomes the shortcomings in a single emissive fluorescent probe, since parameters such as optical path length, local probe concentration, photobleaching, and leakage from the cells are irrelevant because both signals come from the probe in exactly the same environment.

To firmly reveal PET in the super molecule and the mechanism of dual emission, we next check its photophysical process in more detail.

Intramolecular PET in ZnPc(α-OPhONa)$_4$

Comparison of the UV-vis absorption maximum shows that the value is increased slightly in the order: 670 nm for ZnPc < 690 nm for ZnPc(α-OPh)$_4$ < 696 nm for ZnPc (α-OPhOH)$_4$ < 704 nm for ZnPc(α-OPhONa)$_4$, the rank matches the electron donating ability of the substituents. It is the bridging oxygen atoms rather than phenyls, however, that make the major contribution to the red shift, since the absorption maximum of 692 nm for ZnPc(α-OCH_3)$_4$ is greater than that of ZnPc(α-OPhOH)$_4$ [11]. This results clearly indicate that the phenyl moieties are not π-conjugated with the Pc unit. The shape of the absorption spectra, on the other hand, remains the same as that of ZnPc, suggesting that –PhOH or PhONa only weakly interacts with ZnPc moiety in their ground states. The molecular mechanics calculation suggests that the phenyl moiety is almost perpendicular to the Pc ring. Based on above results, we conclude that the electron cloud of phenyl units is actually independent from that of

Pc moiety in their ground states, which satisfy the prerequisite for intra-molecular PET.

The fluorescence quantum yield in methanol is 0.25, 0.18 and 0.0030 for ZnPc(α-OPh)$_4$, ZnPc(α-OPhOH)$_4$, and ZnPc(α-OPhONa)$_4$, respectively, which shows that PhONa is a much more effective quencher than PhOH.

The measurement of fluorescence lifetime, as shown in Fig. 3, gives a further support of intra-molecular PET. Both ZnPc(α-OPh)$_4$ and ZnPc(α-OPhOH)$_4$ exhibit the typical mono-exponential decay, ZnPc(α-OPh)$_4$ has a slightly longer fluorescence lifetime (τ_f) of 3.02 than 2.92 ns of ZnPc(α-OPhOH)$_4$. ZnPc(α-OPhONa)$_4$, however, shows bi-exponential behavior. The short-lived component features a τ_f of less than 0.20 ns (detection limit) and is responsible for 86% photons emitted, the long one has a τ_f of 3.22 ns and assume 14% of emission. The τ_f of major emitting species is significantly shortened to less than 6.8% of the value for ZnPc(α-OPhOH)$_4$, due to efficient PET from PhONa moieties to the excited ZnPc sub-unit.

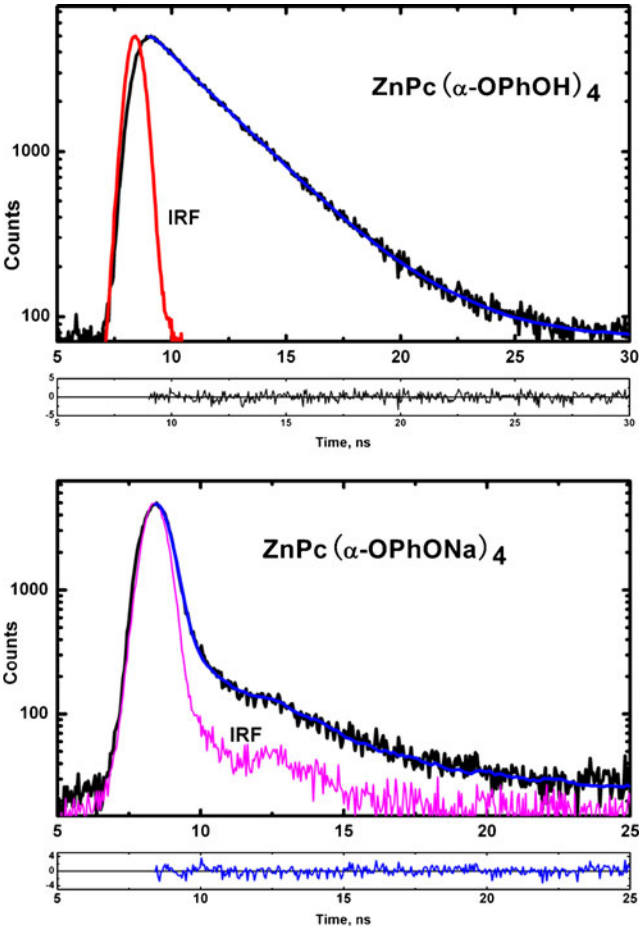

Fig. 3 Time profile of fluorescence decay and fitting curves in methanol with excitation at 672 nm diode laser (50*ps*), the emission was monitored at 710 nm, the concentration of dyes is ca. 5.0 μM. Top: ZnPc(α-OPhOH)$_4$, bottom: ZnPc(α-OPhONa)$_4$. Fitting residues were also included under each figure. Chi squared value is 1.07 and 1.12 for top and bottom case. ZnPc(α-OPhONa)$_4$ was obtained from ZnPc(α-OPhOH)$_4$ in methanol by adding 1.0 mM NaOH

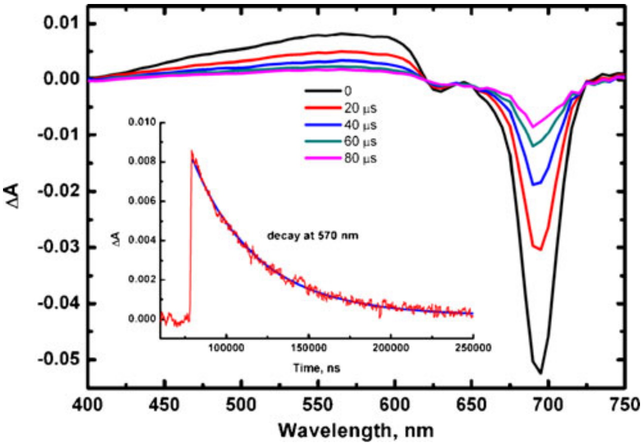

Fig. 4 Transient triplet–triplet absorption of ZnPc(α-OPhOH)$_4$ in argon purged methanol, 10 μM, excitation wavelength 355 nm. Inset shows the decay at 570 nm

Thermodynamic analysis provides us with more firmed evidence that PET can occur while thermal (i.e. ground state) electron transfer is forbidden.

Thermodynamics of PET

The oxidation potential of phenol is known to be $E_{(PhOH/PhOH^{\bullet+})} = 0.60V$ (vs SCE) and the value of phenolate is decreased to 0.40 V [19]. ZnPc(α-OPh)$_4$ exhibits reduction potential at $E_{(ZnPc^{\bullet-}/ZnPc)} = -1.0V$ [20].

The electron transfer in their ground states is not thermodynamically allowed, due to the large positive value of free energy change (ΔG) calculated by $\Delta G_{ET} = E_{ox} - E_{red} - C = 0.40 - (-1.0) - 0.06 = 1.34eV$, in which E_{ox} is the oxidation potential of a donor, E_{red} represents the

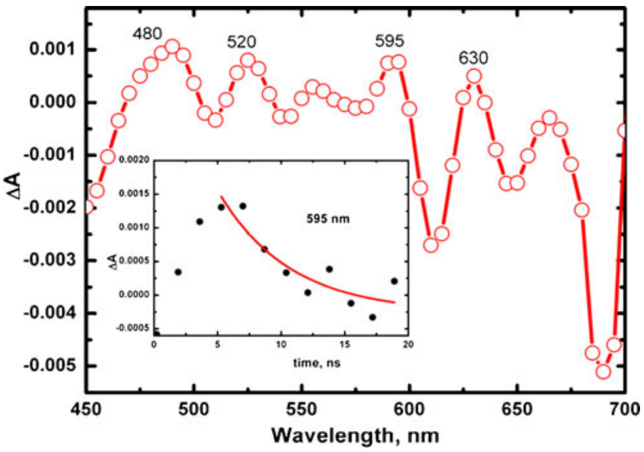

Fig. 5 Transient absorption of ZnPc(α-OPhONa)$_4$ after 10 ns delay of excitation in argon purged methanol containing 1 mM NaOH, 10 μM, excitation wavelength 355 nm. Inset shows the formation and decay at 595 nm

reduction potential of an acceptor, and C is a small constant associated with solvent.

PET from phenolate to S_1 of ZnPc moiety (by the photo excitation of the Pc moiety), on the other hand, is thermodynamically allowed, because its ΔG is a negative value obtained by: $\Delta G_{PET} = \Delta G_{ET} - E_{00}$ (S_1 excitation energy of ZnPc)$=1.34–1.75 = -0.41$ eV, which is more favorable than the case of phenol: $\Delta G_{PET}=-0.21$ eV. PET from Phenolate to T_1 of ZnPc moiety is forbidden, since the energy of the T_1 state is 0.99 eV [21], which is fairly low and suggesting a ΔG of +0.34 eV.

Efficiency and Kinetics of PET

The rate constant of PET (k_{et}) in ZnPc(α-OPhONa)$_4$ can be calculated from the fluorescence quantum yield and lifetime data using Eq. 1, in which Φ_f^0 and τ_f^0 is the fluorescence quantum yield and lifetime of the model compound, ZnPc(α-OPh)$_4$, while Φ_f and τ_f are the values for ZnPc(α-OPhONa)$_4$. k_{et} is thus obtained as 2.29×10^{10} s^{-1} in ZnPc(α-OPhONa)$_4$ and 1.25×10^{8} s^{-1} for (α-OPhOH)$_4$.

$$k_{et} = \tau_f^{-1} - (\tau_f^0)^{-1} = \frac{(\Phi_f^0/\Phi_f) - 1}{\tau_f^0} \qquad (1)$$

Efficiency for PET (Φ_{et}) was calculated to be 99% and 14%, respectively, by using the Φ_f value $\left(\Phi_{et} = 1 - \left(\Phi_f/\Phi_f{}^0\right)\right)$, which indicates that PET is very efficient in ZnPc(α-OPhONa)$_4$. k_f (the rate constant of fluorescence emission) is 0.83×10^{8} s^{-1} for ZnPc (computed by $k_f = \Phi_f/\tau_f$), which is much slower than the rate of PET. k_{isc} (the rate constant of inter system crossing or ISC) of ZnPc is 0.20×10^{9} s^{-1} (Φ_{isc}/τ_f) [11], smaller than 1% of k_{et}. This suggests that triplet generation by ISC in ZnPc(α-OPhONa)$_4$ would be negligible.

Transient Absorption Studies

Transient absorption spectra were recorded in argon saturated methanol solutions upon laser excitation of 355 nm (5 ns pulse). Figure 4 displays the μs-scale spectra for ZnPc(α-OPhOH)$_4$. It exhibited the typical triplet-triplet (T_1-T_n) transient absorptions as reported [22] with abs. maximum at 565 nm. The fitting of transient decay by mono-exponential function gave a lifetime (τ_T) of 38 μs in the absence of oxygen, but it is shortened to 0.11 μs in the air saturated solution, a typical feature of triplet signal.

On the same μs time scale, however, no signal could be detected for ZnPc(α-OPhONa)$_4$, this is due to the efficient quenching of S_1 by PET, so that no remarkable T_1 state was formed. TA absorption on ns scale, on the other hand, could be recorded and is shown in Fig. 5. The difference from Fig. 4 is obvious. The 630, 595 and 480 nm positive absorptions bands are assigned to the anion radical of the phthalocyanine [20], the fitting of decay at 595 nm gives a lifetime of 5.6 ns. The positive 520 nm band is due to phenoxy radical [19, 23]. These positive bands are accompanied by the current occurrence of negative bands due to the bleaching of ground state of ZnPc moiety, indicating that the positive bands of charge separation state is indeed originated from the light excitation of ground state.

Conclusion

The fluorescence of ZnPc(α-OPhOH)$_4$, shows profound dependency on pH values. Very efficient intra-molecular PET occurs in the phenol-substituted zinc phthalocyanine, ZnPc(α-OPhONa)$_4$, upon photoexcitation which quenches its fluorescence. Its conjugate acid, ZnPc(α-OPhOH)$_4$, on the other hand, shows fairly weak PET and therefore highly fluorescent. Upon pH increase in solution containing ZnPc (α-OPhOH)$_4$, the fluorescence is switched off at pH 9.1. Dual emission bands were observed when pH>7, one is attributed to the ZnPc moiety, while the other is from the anion of ZnPc generated by PET. The results suggest that ZnPc(α-OPhOH)$_4$ may be used as a fluorescent pH indicator.

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