

# Reductive Fluorescence Quenching of the Photoexcited Free Base *meso*-Tetrakis (Pentafluorophenyl) Porphyrin by Amines

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**Abstract** Steady state and time resolved fluorescence quenching behaviors of *meso*-Tetrakis (pentafluorophenyl) porphyrin ( $H_2F_{20}TPP$ ) in presence of different aliphatic and aromatic amines have been executed in homogeneous dichloromethane (DCM) solution. At room temperature in DCM, free base ( $H_2F_{20}TPP$ ) shows fluorescence with two distinct peaks at 640 and 711 nm and natural lifetime  $\tau_f = 9.8$  ns which are very similar to that of *meso*-tetraphenyl porphyrin (TPP). Unlike TPP, addition of both aliphatic and aromatic amines to a solution containing  $H_2F_{20}TPP$  results in an efficient decrease in fluorescence intensity without altering the shape and peak position of fluorescence emission. Upon addition of amines there was no change in optical absorption spectra of  $H_2F_{20}TPP$ . The fluorescence quenching rate constants ranged from  $1 \times 10^9$  to  $4 \times 10^9$   $s^{-1}$ , which are one order below to the diffusion control limit, and temperature dependent quenching rate constants yield the activation energies which are found to be order of 0.1 eV. Femto second transient absorption studies reveal the

existence of amine cation radical and porphyrin anion radicals with very short decay time (15 ps). The fluorescence quenching reaction follows Stern–Volmer kinetics. Steady state and time-resolved data are interpreted within general kinetic scheme of Marcus semi-classical model which attributes bimolecular electron transfer process between amines and the lowest excited singlet state of  $H_2F_{20}TPP$ . Calculated internal reorganization energies are found to be in between 0.04 and 0.22 eV. Variation of electron transfer rate as function of free energy change ( $\Delta G^0$ ) points the ET reactions in the present systems are in Marcus normal region. This is the first example of reductive fluorescence quenching of free base neutral porphyrins in homogeneous organic solvent ever known.

**Keywords** Fluorescence quenching · Transient absorption · Electron transfer · Amine · Porphyrin

## Introduction

The porphyrins play central role in different fields of research, which include catalysis, solar energy conversion, the primary process of photosynthesis and the development of advanced functional organic materials [1–3]. When the primary process of photosynthesis is concerned, exploration of the fundamental issues like the movement of charge into or out of the porphyrin macrocycle, the studies of the ground-state and excited-state properties of different porphyrin derivatives are very important as it is influenced by peripheral or central substitutions. The change in absorption spectra and electron donating or electron accepting strength of the porphyrin observed even in non-coplanar systems, such as tetraphenylporphyrin (TPP) and their cation due to the substitution on the phenyl ring are

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usually interpreted in terms of resonative interactions with porphyrin ring [4, 5].

In view of solar energy conversion, numerous projects have been taken up inspired by Nature's delivery of excitation energy into long-distance charge-separated states, [6–8] that involve, for example the manufacturing of the of artificial light-harvesting complexes, [9–11] mimics of the photosynthetic reaction-center [11–13] and molecular optoelectronic devices [14]. In order to address the primary photophysical processes involved in those cases, the photochemistry of tetraphenylporphyrin and its analog have been studied on photoredox reaction of porphyrins in excited triplet states [15, 16]. In relation to the photochemistry of chlorophylls in biological systems investigations to the interaction between photoexcited singlet state of the porphyrin and different electron acceptors have been documented [17, 18]. Nevertheless, porphyrins have been established to manifest selective affinity to tumor cells [19] and the use of porphyrins for photodynamic cancer therapy as a photosensitizer has long been recognized [19, 20]. Due to the success of porphyrin as photosensitizer, studies aimed at understanding the molecular interaction between quencher are of much interest. There are few studies on fluorescence quenching of porphyrin by quinone and nitroaromatics in organic solvents [21, 23] where static quenching partly responsible to the quenching process as weak interaction between porphyrins and electron acceptors in their ground states has been demonstrated [24]. K. Kano et.al reported fluorescence quenching of water soluble anionic porphyrin such as 5-phenyl-5, 10, 15, 20- tris (p-sulfonatophenyl) porphyrin (TPPS<sup>3-</sup>) and 5,10,15,20-tetrakis (4-N-methylpyridyl)porphyrin (TMPyP<sup>4+</sup>) by 9,10 anthraquinone-2,6 disulfonate (AQDS<sup>2-</sup>) and methyl viologen (MV<sup>2+</sup>) [25]. Furthermore, fluorescence quenching studies of porphyrin have been a major issue of porphyrin research on demand by diverse analytical and technological applications, chemical and biological sensors, [26] fluorescent probes, [27] and novel types of imaging process [28]. But fluorescence quenching of free base porphyrin derivatives by electron donors (reductive quenching of the porphyrin siglet state) in homogeneous organic solvent have not been studied although a few cases have been documented elsewhere with its metal counter part.

Similarly, reductive quenchers are not very common and even more rare are reductive quenchers that do not interfere with experiments that involve the absorption of light with 500–800 nm wavelengths. Here we report the amines (e.g TEA, N-ethylpiperidine, N-methylpiperidine, DABCO and aniline) that meet these criteria are to reduce free base meso-tetra(pentafluorophenyl)porphyrin (H<sub>2</sub>F<sub>20</sub>TPP). After H<sub>2</sub>F<sub>20</sub>TPP is excited, there are only one way for the electron to repopulate the HOMO: by photon emission or radiative decay. In the presence of a reductive quencher,

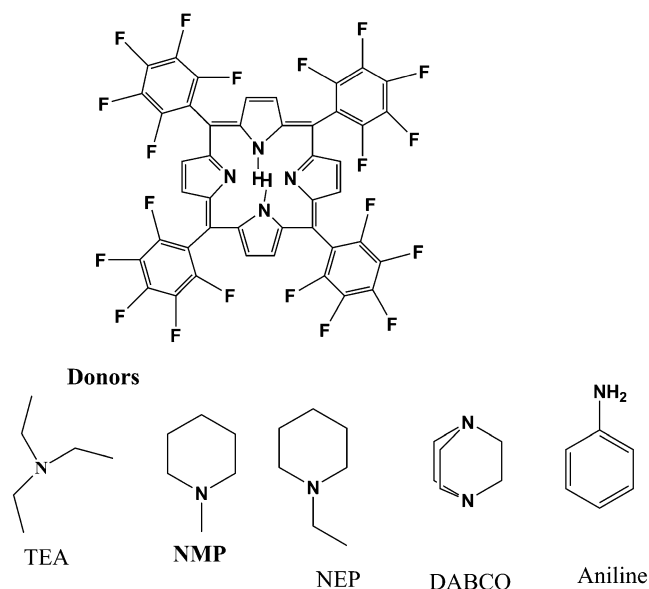
singlet H<sub>2</sub>F<sub>20</sub>TPP is reduced and diminishes the radiative decay. Energy transfer phenomena could also be an alternative pathway to compete with the rates of fluorescence of singlet H<sub>2</sub>F<sub>20</sub>TPP but appearance of zero overlapping of the absorption of amines and emission spectra of H<sub>2</sub>F<sub>20</sub>TPP completely ruled out the possibility of energy transfer to occur. Described here for the first time, a very efficient reductive fluorescence quenching of free base H<sub>2</sub>F<sub>20</sub>TPP by TEA, NEP, NMP, DABCO and aniline is reported and analyzed within Marcus model of electron transfer theory.

## Experimental section

**Materials** The compounds 5,10,15,20-Tetrakis-(phenyl)-porphyrin (TPP) 5,10,15,20-Tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin (H<sub>2</sub>F<sub>20</sub>TPP) was obtained from Porphyrin Systems GbR, Germany and used as received. The amines, triethylamine (TEA), N-methylpiperidine (NMeP), N-ethylpiperidine (NEP), 1,4-diazabicyclo[2.2.2]octane (DABCO) and aniline were from Aldrich, USA. The chemical structures of donors and acceptors are given in Chart 1. The solvent dichloromethane (DCM) (E. Merck) of spectroscopic grade was used.

**Spectroscopic studies** All Uv/vis spectra were recorded using Cintra 10e UV/VIS spectrophotometer (GBC). Spectroscopic titrations were done taking micromolar solutions of H<sub>2</sub>F<sub>20</sub>TPP in DCM and amines concentrations

### Acceptor: H<sub>2</sub>F<sub>20</sub>TPP



**Chart 1** Chemical structures of the donors (aliphatic amines and aniline) and acceptor (H<sub>2</sub>F<sub>20</sub>TPP) used in the present study

were kept up to 0.5 molar. All steady state fluorescence spectra were recorded at room temperature by Fluorolog-3 spectrofluorometer of Horiba Jobin Yvon exciting 596 nm. The time-resolved fluorescence measurements were carried out using a diode laser based time-correlated single-photon counting (TCSPC) spectrometer (Model-5000U), Horiba Jobin Yvon, UK. A 490 nm diode laser with 1 MHz repetition rate was used for the sample excitation. A photomultiplier tube (PMT)-based detector (TBX4, IBH) was used for the detection of the emitted photons through the monochromator. All quenching (steady state and time resolved) experiments were done in DCM solvent with  $\sim 2 \times 10^{-5}$  M concentration of  $H_2F_{20}TPP$ .

**Electrochemical measurements** The oxidation potentials of amines and reduction potential of  $H_2F_{20}TPP$  were determined in DCM solvent by a cyclic voltammetric technique using computer control CHI 620C Instrument.  $TBAClO_4^-$  was used as the supporting electrolyte. Pt as auxiliary electrode and a standard calomel reference electrode were used in the electrochemical measurements.

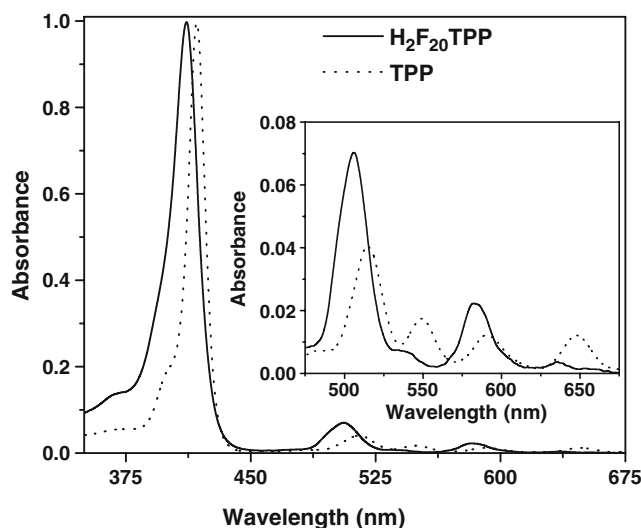
#### Transient absorption measurement

Transient absorption spectra were examined by using femtosecond pump-probe experiments. The samples were excited at 404 nm by second harmonic of an amplified mode-locked Ti:Sapphire laser (Spitfire and Tsunami, Spectra-Physics). Excitation intensity was  $\sim 200$   $\mu W$  with the repetition rate of 0.5 kHz by using a chopper (Model 3501, New Focus, Inc.). Excitation intensity was measured by calibrated power meter (Orion/PD, Ophir). Absorption transients were probed by delayed pulses. The white-light continuum was generated by focusing fundamental laser pulse (800 nm) into a  $D_2O$  cell and detected by a polychromator-CCD combination (Spectra Pro-275 and Spec-10, Acton Research Co. and Princeton Instruments). As a measure of transient absorption we used the differential optical density ( $\Delta OD$ ) defined as the following:  $\Delta OD = \log(I_{OFF}/I_{ON})$ , where  $I_{OFF}$  and  $I_{ON}$  are transmitted white-light intensity in the absence and the presence of the pump pulse, respectively. A temporal dispersion of the white-light continuum was corrected for the transient absorption spectra.

## Results

### Absorption spectra

The electronic absorption spectra of  $H_2F_{20}TPP$  in dichloromethane solution (Fig. 1) show the main characteristic of

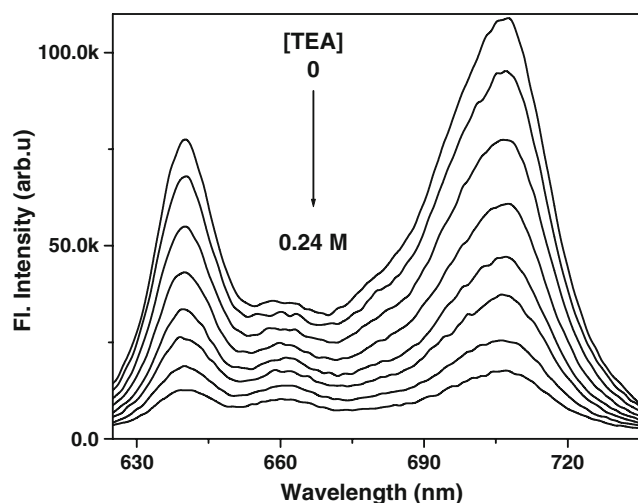


**Fig. 1** Absorption spectra of  $H_2F_{20}TPP$  and TPP in DCM solvent and Insert is the enlarge part of Q bands

parent tetra-phenylporphyrin, which feature intense Soret band at 411 nm ( $\epsilon = 321 \times 10^3$   $\text{mol}^{-1} \text{cm}^{-1}$ ) and four less intense Q-bands at 505 ( $\epsilon = 22 \times 10^3$   $\text{mol}^{-1} \text{cm}^{-1}$ ), 535 ( $\epsilon = 1.6 \times 10^3$   $\text{mol}^{-1} \text{cm}^{-1}$ ), 580 ( $\epsilon = 6 \times 10^3$   $\text{mol}^{-1} \text{cm}^{-1}$ ) and 635 nm ( $\epsilon = 0.8 \times 10^3$   $\text{mol}^{-1} \text{cm}^{-1}$ ) respectively. A systematic blue shift of 8–10 nm for all bands was observed with respect to absorption bands of TPP and which is due to the electron withdrawing character of the peripheral pentafluorophenyl substituent. However, successive addition of amines in the  $H_2F_{20}TPP$  solution in DCM brings no change in absorption spectra of  $H_2F_{20}TPP$ , even in 4:1 (TEA:DCM) solution no change of absorption spectra was observed. This result prevails that there is no ground state interaction between  $H_2F_{20}TPP$  and amines and possibility of the formation of ground state complex is completely ruled out.

### Steady state fluorescence spectra

Photoexcitation of  $H_2F_{20}TPP$  in DCM at any of the absorption band results in the formation of singlet-excited  $\pi\pi^*$  states of  $H_2F_{20}TPP$ , which show normal fluorescence peaking at 640 and 707 nm respectively. The fluorescence quantum yield  $\phi_f = 0.058$  calculated according to secondary standard method is little less than that of TPP where as lifetime values  $\tau_0 = 9.8$  ns are in good agreement with that of TPP [29]. However, upon addition of aliphatic as well as aromatic amines in DCM solution of  $H_2F_{20}TPP$  ( $\sim 5 \times 10^{-5}$  M), the fluorescence of  $H_2F_{20}TPP$  quenches without any deformation in fluorescence spectral shape, even at highest concentration of the amines used, whereas similar experiment does not show any quenching of the fluorescence of TPP. Thus no exciplex formation is observed in the present systems. A representative plot of fluorescence quenching of  $H_2F_{20}TPP$  as function of TEA is given in Fig. 2. As shown in Fig. 3, a strong linear

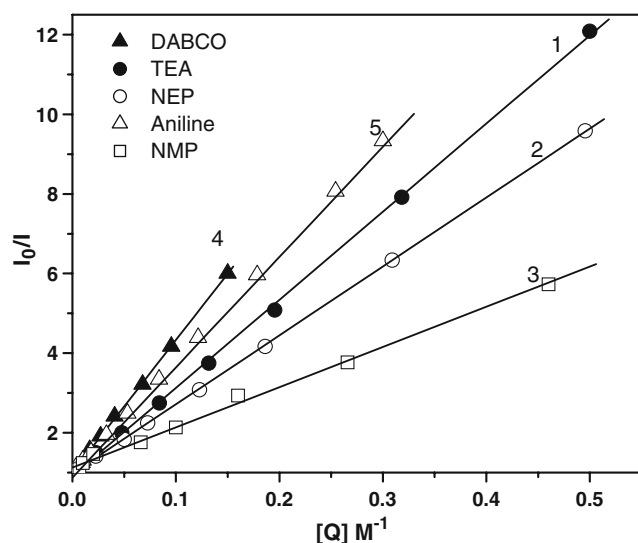


**Fig. 2** Change of fluorescence spectra of  $H_2F_{20}TPP$  as function of TEA concentration

relationship of the relative fluorescence intensities of  $H_2F_{20}TPP$  at any given wavelength is obtained for all amines up to 99% of quenching with increasing concentration of quenchers and it is in agreement with the Stern–Volmer bimolecular kinetic model as below,

$$\frac{I_0}{I} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \quad (1)$$

where  $I_0$  and  $I$  are the relative fluorescence intensities of  $H_2F_{20}TPP$  without and with the amines concentration  $[Q]$ ,  $K_{SV}$  is the Stern–Volmer constant,  $\tau_0$  is the natural fluorescence decay time of  $H_2F_{20}TPP$  and  $k_q$  is quenching rate constant.  $K_{SV}$  values obtained for different aliphatic amines corresponds the electron donor strength of amines. Quenching



**Fig. 3** Stern–Volmer (SV) plots based on change in fluorescence intensity by using Eq. 1 for the present  $H_2F_{20}TPP$  and amine pairs in DCM solvent. (1) TEA, (2) NEP, (3) NMP, (4) DABCO, (5) Aniline

efficiencies observed (Table 1) are considerably high and calculated  $k_q$  values are one order less than diffusion controlled limit. Furthermore, for aniline, an aromatic amine  $K_{SV}$  value is  $\sim 3$  fold higher than that of aliphatic amine of same donor strength.

#### Time resolved fluorescence studies

The fluorescence lifetime ( $\tau$ ) of  $H_2F_{20}TPP$  sharply decreases by successive addition of the amines in DCM solution. Figure 4 shows a representative fluorescence decay profile of  $H_2F_{20}TPP$  as function of the concentration of DABCO. Kinetic plots according to Eq. 2 were strictly linear in all cases (Fig. 5) and afforded the quenching rate constants in Table 2.

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \quad (2)$$

Fluorescence decay remains single exponential in all cases. Moreover, values of  $(I_0/I)$ , from steady state fluorescence measurements, match  $(\tau_0/\tau)$  ratios throughout the concentration range. This result again excludes the formation of exciplex and indicates the quenching phenomena is purely dynamic in nature i.e. quenching is occurred solely by collisional deactivation of singlet excited state of  $H_2F_{20}TPP$ . Comparison of the  $K_{SV}$  values in Table 1 with corresponding values of measured oxidation potentials  $E_{OX}$  of the quenchers provides information regarding the participation of electron in the quenching process.

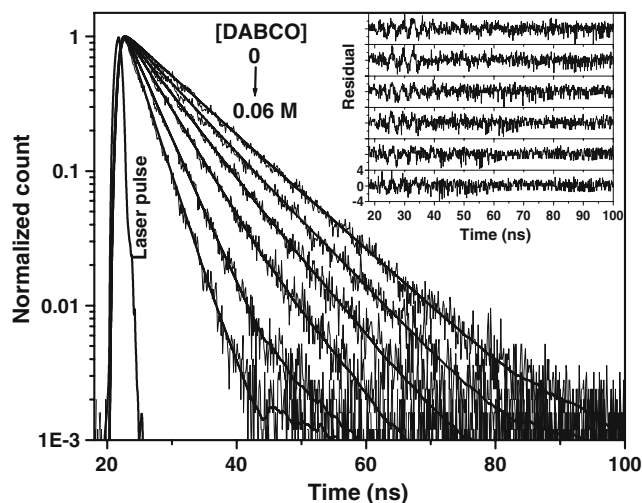
#### Temperature dependent quenching

The temperature dependence of the bimolecular quenching rate constants was evaluated for all aliphatic amines. In all cases, upon increasing the temperature from 276 to 310 K,  $K_{SV}$  values increase. Due to the limitation in measuring temperature dependent lifetime in our lab, we have taken the ratio metric lifetime change along with the fluorescence

**Table 1** Oxidation potential of amines,  $(\Delta G^0)_{approx}$  and Stern–Volmer constants based on fluorescence ( $K_{SV}(I_0/I)$ ) and lifetime ( $K_{SV}(\tau_0/\tau)$ ) measurements of  $H_2F_{20}TPP$  with variable concentration of amines respectively

Amine	$E_{OX}$ (V)	$-(\Delta G^0)_{approx}$ (eV)	$K_{SV}(I_0/I)$ ( $M^{-1}$ )	$K_{SV}(\tau_0/\tau)$ ( $M^{-1}$ )
TEA	0.89	0.35	21.1	20.7
NEP	1.0	0.25	17.8	17.1
NMP	1.1	0.15	10.1	10.1
DABCO	0.74	0.5	36.8	38.9
Aniline	1.1	0.15	28	27.5

$(\Delta G^0)_{approx}$  = thermodynamic free energy excluding Coulomb term in (3)



**Fig. 4** Fluorescence decay curves of  $\text{H}_2\text{F}_{20}\text{TPP}$  as function of the concentration of DABCO in DCM at room temperature

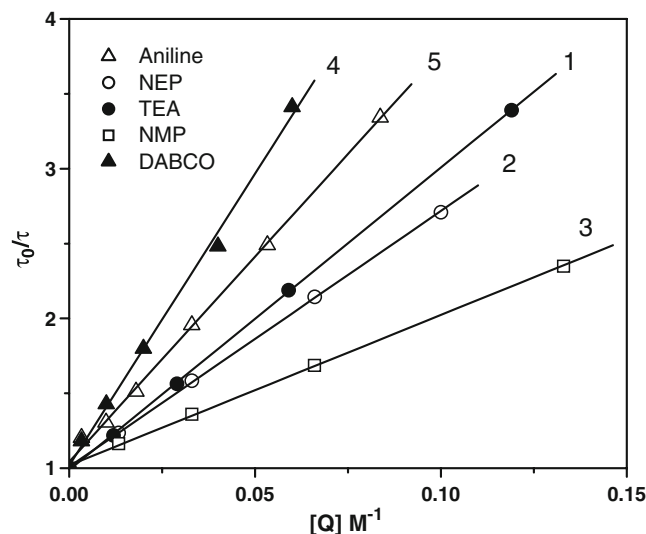
intensity change on increasing temperature. The fluorescence intensities of  $\text{H}_2\text{F}_{20}\text{TPP}$  decreases on increasing temperature and similar proportion of decrease in lifetime is taken into account to calculate temperature dependent quenching rate constant ( $k_q$ ) and the calculated quenching rate constant is found to increase with temperature. The resulting Arrhenius plots [ $\ln(k_q)$  versus  $1/k_bT$ ] were found to be linear over the examined temperature range (5–37 °C) (Fig. 6). They provided a pre-exponential factor  $A$  of the order  $\sim 10^{10}$  and an activation energy ( $\Delta G^*$ ) (Table 2).

#### Picosecond transient absorption studies

The electron transfer reaction is evidently needed to account for both the appearance of product radicals. Assuming the fact of electron transfer from amines to singlet excited  $\text{H}_2\text{F}_{20}\text{TPP}$ , we have carried out the transient absorption measurement using femto second pump-probe technique. The transient absorption measurements were carried out for  $\text{H}_2\text{F}_{20}\text{TPP}$  and TEA system in DCM solution. Since the Q band of  $\text{H}_2\text{F}_{20}\text{TPP}$  has wide range absorption in between 450 and 660 nm and moderately strong fluorescence above 620 nm, contributions from the ground state absorption and stimulated emissions in the transient absorption spectra are inevitable and a more quantitative determination of radical yields is impeded by the quite low absorbance of these transients, the overlap with the ground state absorption and fluorescence emission of  $\text{H}_2\text{F}_{20}\text{TPP}$ . An effort has been taken to minimize the effect of the stimulated emissions using quite high concentrations of the amine with respect to  $\text{H}_2\text{F}_{20}\text{TPP}$  concentration resulting to a large extent of fluorescence quenching. In contrast, presence of amine does not change the ground state absorbance of Q band of  $\text{H}_2\text{F}_{20}\text{TPP}$  and thus

minimization of ground state depletion in transient is almost unavoidable. Hence to minimize the ground state depletion, a very low concentration ( $1 \times 10^{-5}$  M) of  $\text{H}_2\text{F}_{20}\text{TPP}$  was used in DCM solutions which in turn again reduces the total yield of radicals. However, pumping was done at 404 nm, a high energy tail of B band (Soret band). Even though observed transient absorption spectra were found to be a superposition of the stimulated emissions, depletion of the ground state of  $\text{H}_2\text{F}_{20}\text{TPP}$ , and the absorption signals of the transients. Thus the absorption signals for the transients produced following ET reactions could be the signature of the presence of the radicals quantitatively.

Typical femto second time-resolved transient absorption spectra as obtained for  $\text{H}_2\text{F}_{20}\text{TPP}$  and TEA system in DCM with TEA concentration of about  $1 \times 10^{-2}$  M are shown in Fig. 7. An absorption band with a peak around 450 nm appears immediately after the excitation pulse. This absorption band is attributed to the TEA cation radical [30]. However, the contributions from the ground state absorption were observed all over the transient absorption signal and stimulated emission could also be found in the 640–750 nm region as this is the spectral region which overlaps with the fluorescence spectra of the  $\text{H}_2\text{F}_{20}\text{TPP}$ . In the transient absorption spectra, a broad absorption band could be resolved by nonlinear curve fitting technique with peak position in the spectral region at about 550 nm. This we attribute to the  $\text{H}_2\text{F}_{20}\text{TPP}$  anion radical. To the best of our knowledge, the absorption spectra of the  $\text{H}_2\text{F}_{20}\text{TPP}$  anion radicals are not reported in the literature. As seen from Fig. 7, the absorption signal for the TEA cation radicals, and the broad absorptions at about 550 nm due to



**Fig. 5** Stern–Volmer (SV) plots based on change in lifetime by using Eq. 2 for the present  $\text{H}_2\text{F}_{20}\text{TPP}$  and amine pairs in DCM solvent. (1) TEA, (2) NEP, (3) NMP, (4) DABCO, (5) Aniline

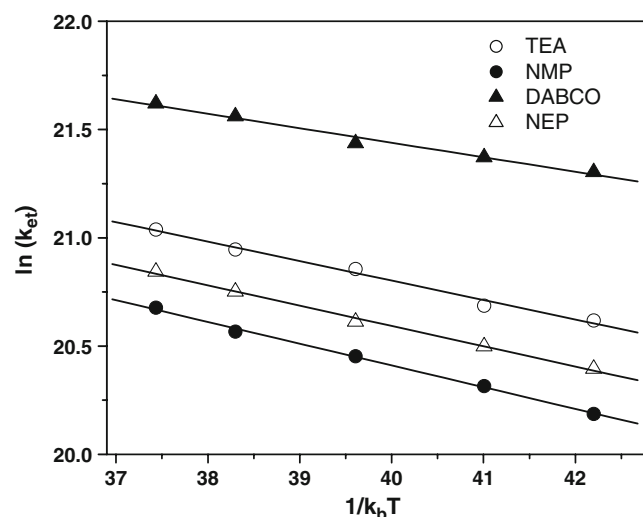
**Table 2** Estimated diffusion coefficients, rate constants, reorganizational energies, free energy changes, activation energies and frequency factors for different amine- H<sub>2</sub>F<sub>20</sub>TPP pairs

Amine	$D_{DA} \times 10^9$ , $m^2 s^{-1}$	$k_d \times 10^{-10} M^{-1} s^{-1}$	$k_q \times 10^{-9} M^{-1} s^{-1}$	$k_{et} \times 10^{-9} M^{-1} s^{-1}$	$\lambda^a$ (eV)	$\lambda_s^b$ (eV)	$\lambda_{in}$ (eV)	$\Delta G^0$ (eV)	$\Delta G^*$ (eV)	$A \times 10^{-10} s^{-1}$
TEA	2.25	1.63	2.11	1.05	1.14	0.95	0.2	-0.5	0.09	3.9
NEP	2.25	1.63	1.74	0.85	1.02	0.95	0.07	-0.4	0.094	3.7
NMP	2.33	1.66	1.03	0.52	1.0	0.96	0.04	-0.3	0.10	4.0
DABCO	2.37	1.67	3.96	2.59	1.22	1.0	0.22	-0.65	0.067	2.95

<sup>a</sup> Calculated using Eq. 10

<sup>b</sup> Calculated using Eq. 11

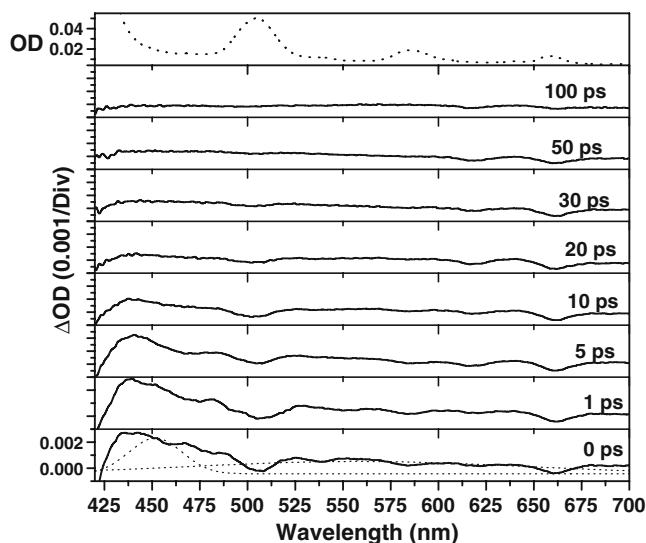
H<sub>2</sub>F<sub>20</sub>TPP radicals gradually reduce as the delay between the pump and probe pulses is increased. Considering the transient absorption signals in the 450 nm region is due to the TEA cation radicals, the lifetime of the cation radicals ( $\tau_{cat}$ ) could be estimated following the decay of these signals. However, the signal strength is too low to estimate the ( $\tau_{cat}$ ) values accurately. Qualitatively, however, it is indicated from the picosecond results that the  $\tau_{cat}$  values of cation radical for these system is about 13 ps. Similarly, considering the 550 nm band as H<sub>2</sub>F<sub>20</sub>TPP radical anion,  $\tau_{an}$  value calculated following the decay of the signal as function of delay is approximated to be 15 ps and it matches with the value found from TEA cation radical within error limit and these values 13–15 ps could be the lifetime of ion-pair states. We attributed these results to ultrafast intermolecular ET from TEA to excited H<sub>2</sub>F<sub>20</sub>TPP. These transient picosecond results thus qualitatively indicate that the excited H<sub>2</sub>F<sub>20</sub>TPP interact with the TEA via ET mechanism.

**Fig. 6** Change of primary electron transfer rate constants as function of temperature for different amine- H<sub>2</sub>F<sub>20</sub>TPP pairs in DCM

## Discussion

### Mechanism for fluorescence quenching

Metal centered porphyrins have been demonstrated as electron donor over long range electron transfer for several systems [31–34]. Ravi Jasuja et al. found water soluble ionic tetrakis(4-*N*-methylpyridyl) porphyrin to demonstrate electron transfer to guanine [35]. Brun and Harriman [36] observed both electron transfer and energy transfer between palladium porphyrins and DNA bound intercalators. Knör. G. observed an electron transfer from halide anion to photo-excited dihydroxy antimony(V) tetraphenylporphyrin cation leading to permanent redox product [37]. But there is no neat evidence where free base porphyrin is acting as electron acceptor in organic solvent. In the present system, quenching of fluorescence of porphyrin is monitored by exciting the porphyrin at ~596 nm and the emission spectrum of H<sub>2</sub>F<sub>20</sub>TPP does not overlap with the

**Fig. 7** Transient absorption spectra of TEA- H<sub>2</sub>F<sub>20</sub>TPP system in H<sub>2</sub>F<sub>20</sub>TPP systems in DCM. *Dotted plot* in upper panel is ground state absorption spectra of H<sub>2</sub>F<sub>20</sub>TPP system

absorption spectrum of the any amines tested. The energy of the first excited singlet state of amines is much higher than that of H<sub>2</sub>F<sub>20</sub>TPP. The lowest energy absorption band of amines is far below than 375 nm where there is no trace of absorption of H<sub>2</sub>F<sub>20</sub>TPP. Therefore, energy transfer from photo-excited H<sub>2</sub>F<sub>20</sub>TPP to the amines simply ruled out as the mechanism for quenching. A close look on redox potentials of the amines and the H<sub>2</sub>F<sub>20</sub>TPP demonstrate that the mechanism of singlet quenching most likely involves with electron transfer between amines and excited singlet of H<sub>2</sub>F<sub>20</sub>TPP. The nature of the electron transfer pathway (i.e., oxidative or reductive quenching of excited porphyrin) can be realized by examining the free energy of the corresponding electron transfer reactions. For reductive quenching of the porphyrin, the thermodynamics driving force of electron transfer from amines to the singlet excited state of porphyrin can be calculated according to well known Rehm–Weller Eq. 3

$$\Delta G^0 = E_{\text{amine/amine}^+} - E_{\text{PFP/PFP}^-} - \Delta E_{00} - \frac{e^2}{4\pi\epsilon r} \quad (3)$$

where  $E_{\text{amine/amine}^+}$  is the oxidation potential for amines,  $E_{\text{PFP/PFP}^-}$  is the reduction potential of the H<sub>2</sub>F<sub>20</sub>TPP,  $\Delta E_{00}$  represents the energy of the singlet excited state of H<sub>2</sub>F<sub>20</sub>TPP and the forth term is the *Coulomb* term which takes into account the electrostatic interaction in the incipient ion-pair after ET with  $e$  is the charge of an electron,  $\epsilon$  the static dielectric constant of the medium, and  $r$  is the distance between the interacting amines and H<sub>2</sub>F<sub>20</sub>TPP. The oxidation potential of the amines are listed in Table 1 which are less than unity and excited singlet state energy ( $\Delta E_{00}$ ) for the porphyrin is 1.94 eV/ (640 nm). An  $\epsilon$  value of 9.1 is considered for dichloromethane. The  $r$  values were considered as the sum of van der Waals radii of the amines and H<sub>2</sub>F<sub>20</sub>TPP assuming them to be spherical molecules. The average value of  $r$  for different amines are calculated to be TEA (3.8 Å), NEP(3.8 Å), NMP(3.6 Å), DABCO (3.5 Å) and Aniline (3.3 Å) and the radius of H<sub>2</sub>F<sub>20</sub>TPP is similarly obtained to be 5.8 Å. Taking the described parameter into account the coulomb term in Eq. 3 is found to be ~0.15 eV. Thus, a thermodynamically favorable electron transfer from the poorest amine (judged by oxidation potentials) to the excited H<sub>2</sub>F<sub>20</sub>TPP will be anticipated only when the reduction potential of H<sub>2</sub>F<sub>20</sub>TPP,  $E_{\text{PFP/PFP}^-}$  is less than 1.33 V and the reduction potential of H<sub>2</sub>F<sub>20</sub>TPP is measured to be 0.7 V in DCM and it matches very well to the value reported elsewhere [38]. Hence, the ET reaction between poorest amine and singlet excited H<sub>2</sub>F<sub>20</sub>TPP pair is exothermic by -0.3 eV and thus the energetically favorable ET is proposed from amine to singlet excited state of H<sub>2</sub>F<sub>20</sub>TPP. The calculated Gibbs free energy (thermodynamic driving force) change ( $\Delta G^0$ ) associated with the proposed ET reaction for different

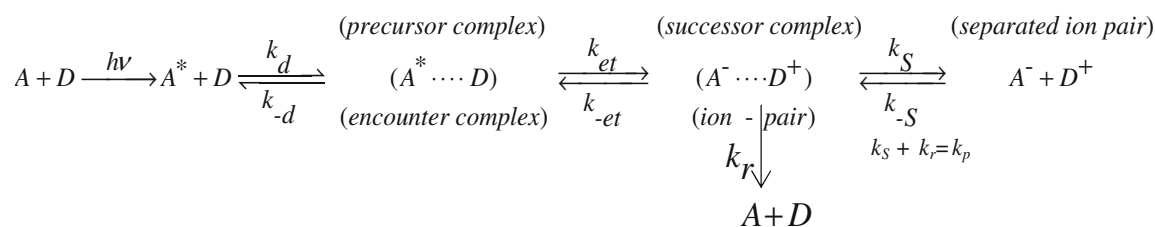
amines—H<sub>2</sub>F<sub>20</sub>TPP pairs along with other linked parameters was given Table 2.

### Quenching of *meso* substituted free base porphyrin

The quenching of the fluorescence of H<sub>2</sub>F<sub>20</sub>TPP is observed in different aliphatic and aromatic amines but no quenching is observed with other base like pyridine and different derivatives of pyridine. No other *meso* substituted functionalized free base porphyrin derivatives (e.g. 5,10,15,20-Tetrakis-(4-pyridyl)-porphyrin, 5,10,15,20-Tetrakis-(3-pyridyl)-porphyrin, 5,10,15,20-Tetrakis-(2-pyridyl)-porphyrin, 5,10,15,20-Tetrakis-(4-cyanophenyl)-porphyrin, 5,10,15,20-Tetrakis-(4-hydroxyphenyl)-porphyrin, 5,10,15,20-Tetrakis-(4-carboxyphenyl)-porphyrin, 5,10,15,20-Tetrakis-(4-methoxyphenyl)-porphyrin, 5,10,15,20-Tetrakis-(4-aminophenyl)-porphyrin,) show fluorescence quenching except H<sub>2</sub>F<sub>20</sub>TPP. Fluorination of phenyl hydrogen of H<sub>2</sub>F<sub>20</sub>TPP does not change much of spectroscopic properties except systematic blue shift of both Soret and Q bands as well as (0,0) fluorescence peak but huge positive shift in its reduction potential (~0.4 V) which makes it as a good oxidizing agent for amines. Perhaps this is the first example of any kind of free base porphyrin showing the reductive fluorescence quenching in organic solvent. This reductive fluorescence quenching behavior of H<sub>2</sub>F<sub>20</sub>TPP can be used for making amine sensor and attempts are under taken in our lab using monolayer of H<sub>2</sub>F<sub>20</sub>TPP molecule. However, to explore the fundamental aspects of this reductive quenching different parameters are analyzed within the framework of Marcus ET theory [39–41].

### Diffusion and quenching parameters

The photoinduced ET from a ground state donor (D) (amines) to an excited state acceptor (A) (H<sub>2</sub>F<sub>20</sub>TPP) is rationalized by the standard free energy change,  $\Delta G^0$ , for the ET reaction. Based on the described experimental evidences (*vide supra*), ET is concluded to be responsible for the fluorescence quenching in the present systems and the relevant rate constants for ET are estimated by employing the mechanistic Scheme 1. In Scheme 1, an encounter complex, (A\*...D) of suitable reorganization is formed by the diffusion of excited acceptor (A\*) and the ground state donor (D) molecules and ET occurs forming the ion-pair state (A<sup>-</sup>...D<sup>+</sup>). The relevant parameters,  $k_d$  and  $k_{-d}$  are the diffusion-controlled rate constants for the formation (second order) and dissociation (first order) of the encounter complex, (A\*...D),  $k_{et}$  and  $k_{-et}$  are the first-order (forward ET) rate constants for charge separation in the “precursor complex” and charge recombination (reverse ET) the “successor complex”, respectively.  $k_S$  is the first-

**Scheme 1**

order rate constant for the dissociation of the “successor complex”, and  $k_r$  is the first order rate constant for reversible electron transfer to ground state reactants.  $k_{-S}$  is the rate constant associated with the diffusion of charge-separated species to re-gain ( $A^- \cdots D^+$ ). Often, the occurrence of this back process is supposed to be slender in a polar solvent such as DCM and from energetic point of view the back electron transfer (reverse ET,  $k_{-et}$ ) is also unlikely process [42]. Thus, it can safely be assumed that  $k_p$ , the sum of all the rate constants involved to cease the existence of the ( $A^- \cdots D^+$ ) state is much higher than  $k_{-et}$  i.e.  $k_p \gg k_{-et}$ . Hence, in steady-state conditions the observed bimolecular quenching constant can be derived as follow

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{Kk_{et}} \quad (4)$$

where  $K$  ( $k_d/k_{-d}$ ) is the diffusional equilibrium constant for the encounter complex formation and can be estimated using Fuoss–Eigen model [43]

$$K = \frac{4}{3} \pi R_{DA}^3 N_A \times \exp\left(\frac{e^2}{4\pi\epsilon\epsilon_0 kTR_{DA}}\right) 1000 \quad (5)$$

In Eq. 5  $N_A$  is the Avogadro’s number,  $R_{DA}$  is the separation between donor and acceptor in the encounter complex. For neutral molecules diffusion occurs freely in homogeneous solution and the exponential term vanishes reducing the Eq. 5 to Eq. 6

$$K = \frac{4}{3} \pi R_{DA}^3 N_A \times 1000 \quad (6)$$

Thus taking the different donor acceptor distances, values for  $K$  are estimated for all donor-acceptor pairs and which are in the range of 1.9 to 2.23 mol<sup>-1</sup> dm<sup>3</sup> for the present amines and H<sub>2</sub>F<sub>20</sub>TPP systems. In order to estimate  $k_d$  the diffusion-controlled rate constants associated to the bimolecular quenching reactions, diffusion coefficient  $D$  of the reactants were calculated according to the following Stokes–Einstein equation,

$$D = \frac{kT}{6\pi\eta r} \quad (7)$$

where  $k$  is the Boltzmann constant and  $\eta$  (0.423 cp) is the kinematic viscosity of DCM at 300 K and  $r$  is the radii of

the molecules. Taking the said radii of respective donors and acceptor (5.8 Å) the diffusion coefficient for each donor-acceptor pairs ( $D_{AD} = D_A + D_D$ , diffusion coefficient of donor ( $D_D$ ), diffusion coefficient acceptor ( $D_A$ )) are calculated at room temperature and listed in Table 2. In steady state picture, time independent Smoluchowsk equation (as in Eq. 8) is used to assess the diffusion-limited rate constant

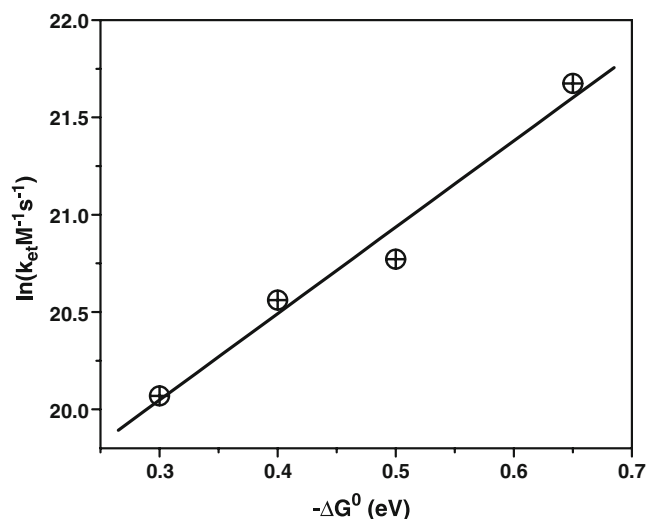
$$k_d = 4\pi R_{DA} N_A D_{DA} \times 10^{-3} \quad (8)$$

where  $N_A$  is Avogadro number. The diffusion-controlled rate constants at room temperature were calculated for all donor-acceptor systems and recorded in Table 2. In each case it was found that the diffusion-controlled rate constants are bit higher than the observed quenching rate constants of the respective donor-acceptor pairs. Hence, primary electron transfer rate constant  $k_{et}$  is calculated from Eq. 4 and placed in Table 2.

#### Marcus theory and quenching parameters

In general activation-controlled electron transfer rate constant is expressed by Arrhenius type of equation [44] as

$$k_{et} = A \exp\left(\frac{-\Delta G^*}{k_b T}\right) \quad (9)$$



**Fig. 8** The change of primary electron transfer rates with thermodynamic free energy for different aliphatic amine and H<sub>2</sub>F<sub>20</sub>TPP systems



where  $A$  is the frequency factor and  $\Delta G^*$ , the energy of activation for the ET process. From temperature dependent rate constant we have found  $A$  to be the order of  $10^{10} \text{ s}^{-1}$  (Table 2) which matches nicely with solution phase collision frequency [44] and  $\Delta G^*$  for different donor and  $\text{H}_2\text{F}_{20}\text{TPP}$  system (Table 2). However, by use of Marcus theory [43], the activation energy can be expressed through the exergonicity of the reaction as.

$$\Delta G^* = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \quad (10)$$

where  $\Delta G^0$  is the free energy change for the ET reaction and  $\lambda$  is total reorganization energy which includes solvent reorganization energy ( $\lambda_s$ ) and internal reorganization energy ( $\lambda_{in}$ ), energy for the intramolecular bond length and bond angle changes of A-D system during electron transfer. Now, putting  $\Delta G^0$  and  $\Delta G^*$  values on Eq. 10 we calculate total reorganization energy  $\lambda$  which is about 1 eV and it is found to be bigger than the thermodynamic free energy i.e.  $-\Delta G^0 < \lambda$  for all cases (Table 2). As shown in Fig. 8, the rate constants increase on increasing free energy of reaction for aliphatic amines studied and  $\text{H}_2\text{F}_{20}\text{TPP}$  system and it claims that the ET reaction for the present D-A systems falls in the Marcus normal region.

In order to have an idea about the internal reorganization energy ( $\lambda_{in}$ ), first we calculated  $\lambda_s$  on the assumption of nonequilibrium polarization of the medium and employing the dielectric continuum model for the solvent, as proposed by Marcus [42].

$$\lambda_s = e^2/4\pi\epsilon_0 \left\{ \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{2R_{DA}} \right\} \left\{ \frac{1}{n^2} - \frac{1}{\epsilon} \right\} \quad (11)$$

where  $r_D$  and  $r_A$  are the radius of the donor and acceptor respectively,  $R_{DA}$  is the separation between the donor and acceptor in the encounter complex,  $n$  is the refractive index, and  $\epsilon$  is the dielectric constant of the solvent. Hence employing the  $r_D$ ,  $r_A$  and  $R_{DA}$  values for specific donor acceptor combination  $\lambda_s$  is calculated and listed in Table 2. Hence  $\lambda - \lambda_s$  gives the values for  $\lambda_{in}$  for each donor–acceptor combination and were found to be in between 0.04 to 0.22 eV, little lower than the usually observed values (0.2–0.4 eV) for normal organic systems [45]. Interestingly, the  $\lambda_{in}$  value for DABCO- $\text{H}_2\text{F}_{20}\text{TPP}$  system is bit higher than other amine- $\text{H}_2\text{F}_{20}\text{TPP}$  system which indicates that intrinsic barrier for ET is relatively high for DABCO although the oxidation potential is less. It is worthy to note here that DABCO shows stereoelectronic effect on ET process but in the present system there is no such indication is observed. For aniline, an aromatic amine the rate of the reaction is quite higher (not shown in table) with respect to available thermodynamic free energy in comparison with the aliphatic amines. This may be due to the difference in interaction

of aliphatic amines and aromatic amines with excited states of acceptor. The aliphatic amines donate electrons through their lone pair orbital and are expected to interact in a different manner than aromatic donors. However, a systematic study with varying oxidation potential for different aromatic amines is planned in order to explore the mechanistic aspects of reductive fluorescence quenching in view of electron transfer reaction where free base porphyrin is a sensitizer.

## Conclusion

In summary, the data described here demonstrated that the singlet excited state of  $\text{H}_2\text{F}_{20}\text{TPP}$  is quenched by aliphatic as well as aromatic amines. This quenching mechanism is attributed to be reductive in nature i.e. electron transfer occurs from ground state amines to excited  $\text{H}_2\text{F}_{20}\text{TPP}$  in DCM. This is the first ever example of reductive quenching of free base neutral porphyrin in organic solvent. The primary electron transfer rate constant  $k_{et}$  in the present system nicely correlate with free energy changes ( $\Delta G^0$ ) of ET reactions within the framework of Marcus ET theory in normal region. These results may anticipate in understanding of ET reactions in other free base porphyrin systems and it could explore the possibilities of making optical amine sensor using  $\text{H}_2\text{F}_{20}\text{TPP}$ .

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