Supporting Information
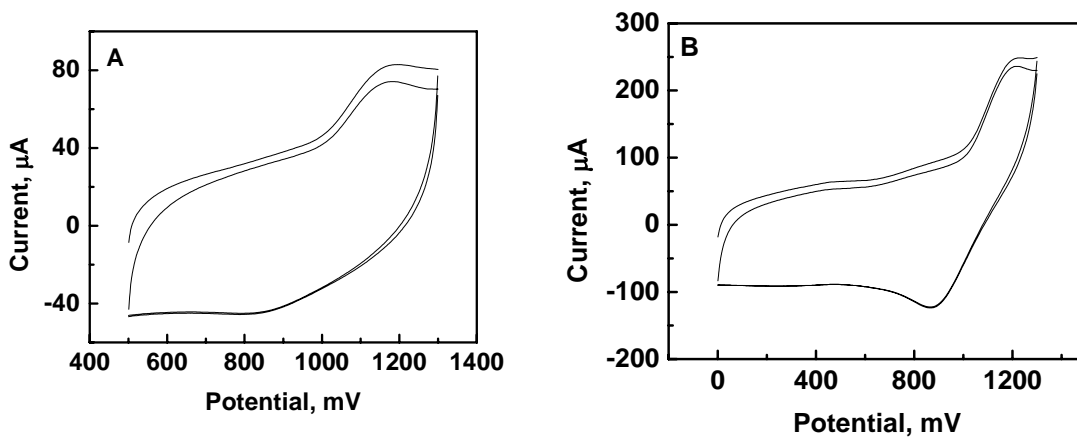
Singlet and Triplet Excited State Interactions and Photochemical Reactivity of Phenyleneethynylene Oligomers

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Figure S1. Oxidative cyclic voltamograms of (A) **OPE-1** and (B) **OPE-2** recorded in acetonitrile. The second wave in each figure represents the measurement recorded sequentially.
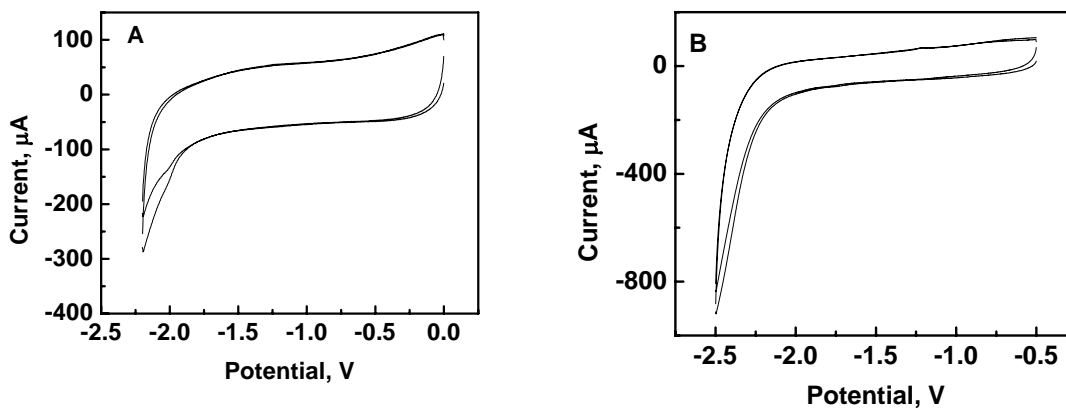
Figure S2. Reductive cyclic voltamograms of (A) **OPE-1** and (B) **OPE-2** recorded in acetonitrile. The second wave in each figure represents the measurement recorded sequentially.
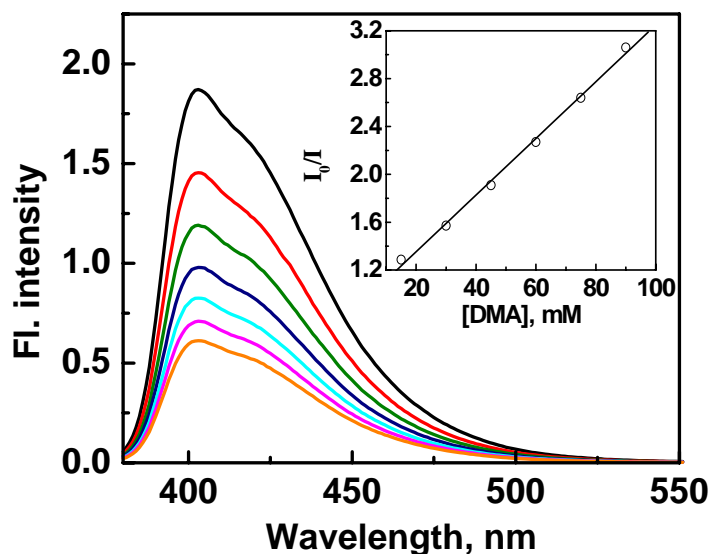
Figure S3. Fluorescence quenching of **OPE-1** by DMA at concentration levels of (a) 0 (b) 15 (c) 30 (d) 45 (e) 60 (f) 75 (g) 90 mM in acetonitrile. λ_{ex} =375 nm. (Optical Density at 375 nm kept as 0.1). Inset shows the Stern-Volmer fit.
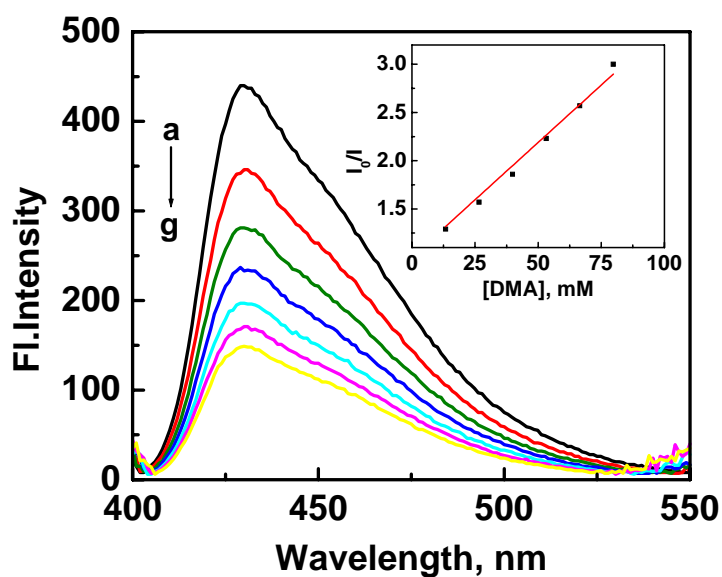
Figure S4. Fluorescence quenching of **OPE-2** by DMA at concentration levels of (a) 0 (b) 13.3 (c) 26.6 (d) 39.9 (e) 53.2 (f) 66.5 (g) 79.8 mM in acetonitrile. λ_{ex} =375 nm. (Optical Density at 375 nm kept as 0.1). Inset shows the Stern-Volmer fit
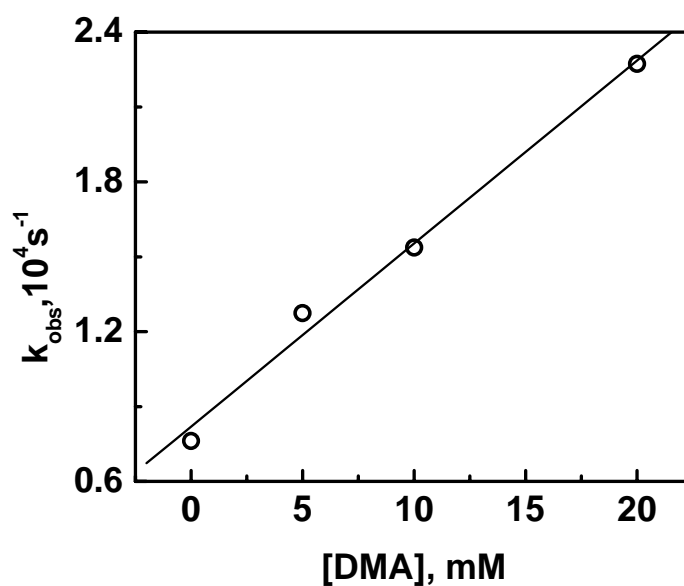
Figure S5. Dependence of pseudo-first-order rate constants for the triplet decay of **OPE-1** on the concentration of DMA. The triplet decay was monitored at 520 nm.
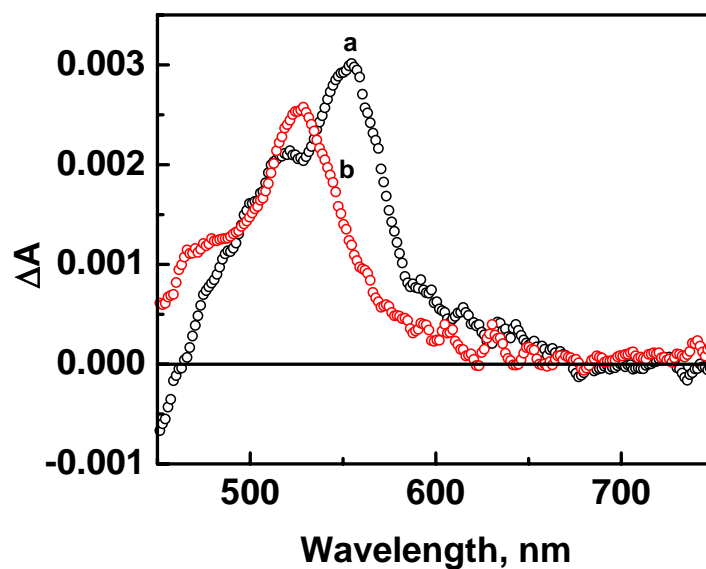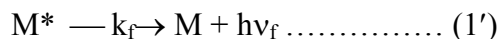

Figure S6. (A) Time-resolved difference absorption spectra recorded after 1 ns following 387-nm laser pulse excitation of **OPE-1** in (a) absence and (b) presence of DMA (0.1 M) in a femtosecond laser flash photolysis apparatus.

Modified Stern-Volmer Plot
Derivation of equation 5

Equation (1′) represents the fluorescence decay of M*

$$M^* \xrightarrow{\;k_f\;} M + h\nu_f \ldots\ldots\ldots\ldots (1')$$

the rate of decay of M* is

$$d[M^*]/dt = -k_f[M^*]\ldots\ldots\ldots\ldots (2')$$

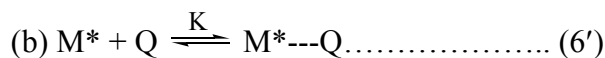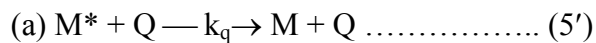$$\Rightarrow [M^*] = [M^*]_0\, e^{-kft} \ldots\ldots\ldots\ldots (3')$$

where $[M^*]_0$ is the initial concentration of M*

The fluorescence intensity, $I \,\alpha\, k_f \int [M^*]dt$

Using equation (3′), $I \,\alpha\, k_f[M^*]_0\int e^{-kft}dt$

$$I \,\alpha\, [M^*]_0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4')$$

In presence of a quencher molecule (Q), the possible interaction between Q and M* are

$$(a)\; M^* + Q \xrightarrow{\;k_q\;} M + Q \ldots\ldots\ldots\ldots (5')$$

$$(b)\; M^* + Q \; \underset{}{\overset{K}{\rightleftharpoons}} \; M^*\text{---}Q \ldots\ldots\ldots\ldots (6')$$

The equilibrium constant K for the formation of complex is

$$K = [M^*\text{---}Q]_0 / [M^*][Q] \ldots\ldots\ldots\ldots (7')$$

If M*---Q is non-fluorescent, the rate of decay of M* is

$$d[M^*]'/dt = -k_f[M^*]' - kq[Q][M^*]'\ldots\ldots\ldots(8')$$

$$\Rightarrow [M^*]' = [M^*]_0'\, e^{-kf + kq[Q]t}\ldots\ldots\ldots\ldots\ldots(9')$$

The fluorescence intensity $I' \,\alpha\, k_f \int [M^*]'dt$

$$I' \,\alpha\, k_f[M^*]_0' / k_f + k_q[Q]$$

$$I' \,\alpha\, [M^*]_0' / (1 + k_q[Q]/k_f)\ldots\ldots\ldots\ldots(10')$$

Dividing (4′) by (10′)

$I/I' = ([M*]_0/[M*]_0')(1+k_q[Q]/k_f)$ …..(11′)

Assuming total excited stated are same in both the cases

$[M*]_0 = [M*]_0' + [M*---Q]_0'$…………..(12′)

$[M*]_0/[M*]_0' = ([M*]_0' + [M*---Q]_0')/([M*]_0' = 1+[M---Q]/([M*] = 1+ K[Q]$………(13′)

Substitute this in equation (11′)

$I_0/I = (1+ K[Q])(1+k_q[Q]/k_f)$

$I_0/I = 1+ (K+kq/kf)[Q]+ K\,kq/kf\,[Q]^2$

$I_0/I = 1+ (K+k_q\tau)[Q]+ K\,k_q\tau\,[Q]^2$………….. (5)