

Supporting Information (SI)

Dynamics of Different Steps of Photopyrolytic Cycle of an Eminent Anticancer Drug Topotecan inside Biocompatible Lyotropic Liquid Crystalline Systems

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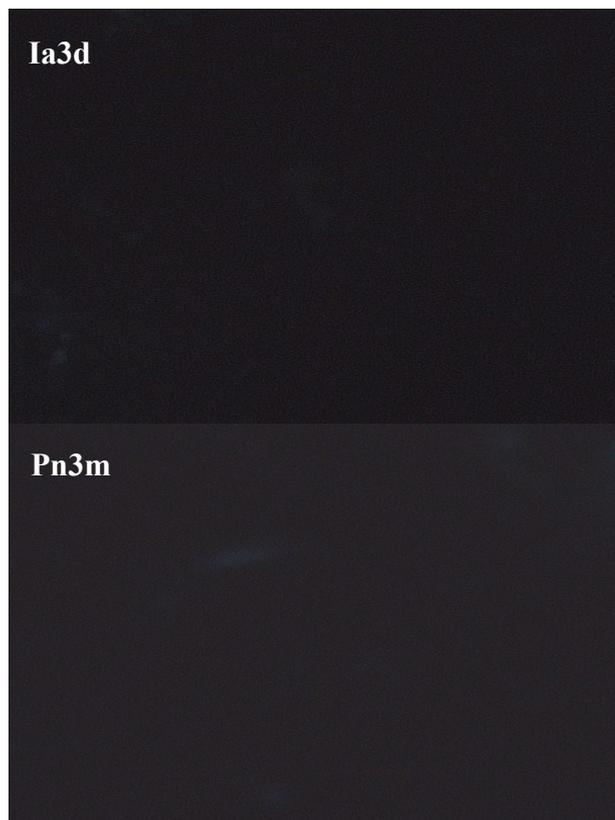


Figure S1: Polarized light microscopy (PLM) images of TPT loaded Ia3d and Pn3m phases. The images have been taken at room (298 K) temperature. The above phases do not exhibit any texture, as they cannot show any birefringence property due to the presence of cubic symmetry of those phases.

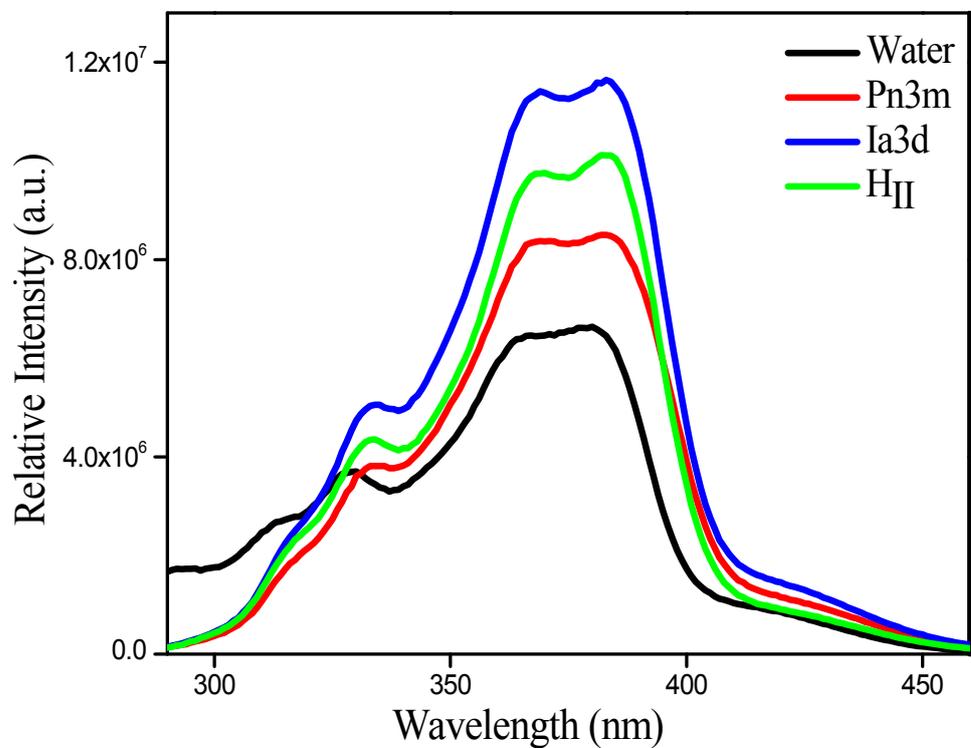


Figure S2: Steady state excitation spectra of TPT in bulk water, and inside different LLC phases. The peaks at ~ 380 nm and shoulder at ~ 409 nm indicates the presence of cationic form and zwitterionic forms of the drug, respectively.

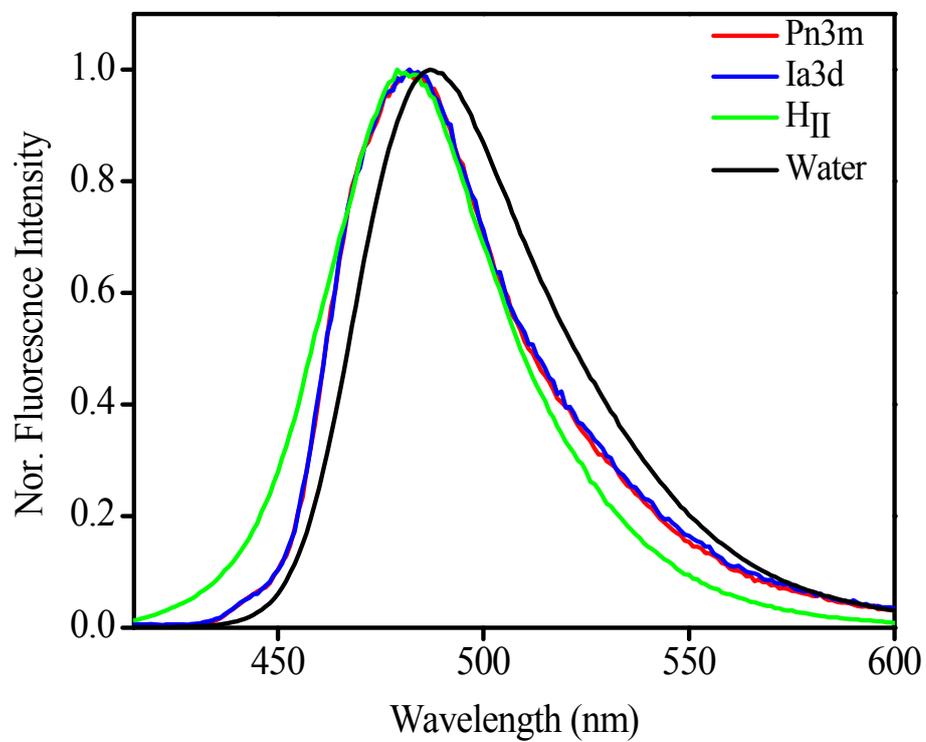


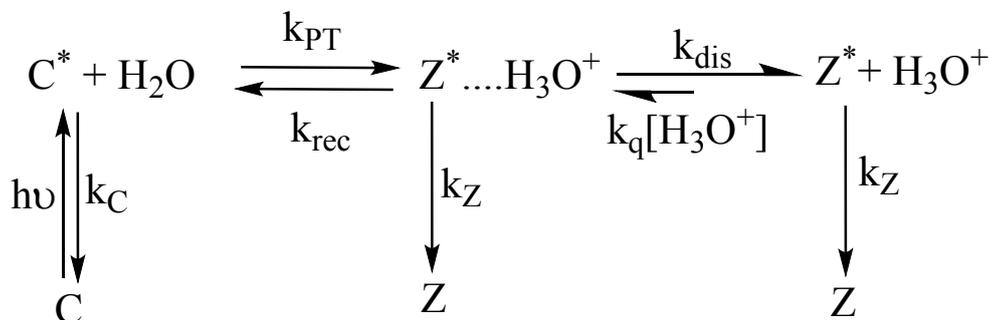
Figure S3: Normalized steady state emission spectra of C-343 in bulk water and inside different LLC phases ($\lambda_{\text{ex}} = 405$ nm).

Table S1: Time-resolved decay parameters (bi-exponential fittings) of cationic ($\lambda_{\text{coll}} = 420$ nm) and zwitterionic ($\lambda_{\text{coll}} = 570$ nm) forms of TPT inside different LLC phases. Excitation wavelength is 375 nm.

Phases	Water (wt %)	λ_{coll} (nm)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	a_3	τ_3 (ns)	τ_{av} (ns)	χ^2
H _{II}	22 wt%	570	-	-	0.47	2.72	0.53	5.26	4.08	1.36
Ia3d	22 wt%	570	-	-	0.6	4.13	0.4	5.91	4.85	1.66
Pn3m	22 wt%	570	-	-	0.45	3.57	0.55	5.59	4.68	1.39
H _{II}	22 wt%	420	0.8	0.351	0.2	1.7	-	-	0.617	1.81
Ia3d	22 wt%	420	0.73	0.202	0.27	1.03	-	-	0.426	2.22
Pn3m	22 wt%	420	0.21	0.255	0.21	1.22	-	-	0.454	1.99

Note S1: Description of Photopyrolytic Scheme of TPT inside LLC Phases:

As we have already mentioned that the time-resolved decay profiles of C^* ($\lambda_{\text{coll}} = 420 \text{ nm}$) and Z^* ($\lambda_{\text{coll}} = 570 \text{ nm}$) form of TPT inside each LLC phase are best fitted by tri-exponential function (Table 1), indicating the presence of three kinetically coupled species in the excited state of TPT.^{1, 2} Out of the three kinetically coupled species one is solvent separated conjugate base ($Z^* \dots H_3O^+$) responsible for the geminate recombination process, which is evident from the asymptotic non-exponential long time fluorescence tail in the decay pattern of C^* -TPT. The other two species are C^* and Z^* form of TPT affirmed from the life time component of C^* form (τ_2 of $\lambda_{\text{coll}} = 420 \text{ nm}$) and Z^* form (τ_3 of $\lambda_{\text{coll}} = 570 \text{ nm}$), respectively (Figure 3, Table 1). Based on this observation, the kinetics of photopyrolytic processes of TPT inside LLC phases can be represented by the following scheme:



The above mentioned kinetic scheme can be described as follows. Initially, the selective excitation ($\lambda_{\text{exc}} = 375 \text{ nm}$) of cationic form (C) of TPT generates excited state C^* form, which primarily starts the photopyrolytic process. Electronically excited C^* molecules subsequently release a proton from the $-OH$ group ($\text{pKa}^* = -2.62$)³ of 6-hydroxy quinoline (A and B ring) moiety of the TPT molecule to the nearby water molecule with the rate constant (k_{PT}), resulting an intimate ion-pair ($Z^* \dots H_3O^+$) formation. This intimate ion pair

($Z^* \dots H_3O^+$) separates into stabilized zwitterionic form (Z^*) and the ejected proton (H_3O^+). In addition to that, the ejected proton and conjugate base (Z^*) may reversibly recombine with the rate constant k_{rec} and regenerate the excited state C^* form of TPT. The solvent stabilized zwitterionic form and ejected proton will hardly undergo reversible ion-pair formation, and hence, the rate constant of this process, i.e., $k_q[H_3O^+]$ can be neglected.

Note S2: Calculation of Rate Constants for Different Steps of Photopyrolytic Processes of TPT:

Based on the proposed kinetic scheme, the time evaluation of the different species can be described by the following coupled differential equations^{1,2}

$$\frac{d}{dt} \begin{bmatrix} C^* \\ Z^* \dots H_3O^+ \\ Z^* \end{bmatrix} = \begin{bmatrix} -m_1 & k_{rec} & 0 \\ k_{PT} & -m_2 & 0 \\ 0 & k_{dis} & -m_3 \end{bmatrix} \begin{bmatrix} C^* \\ Z^* \dots H_3O^+ \\ Z^* \end{bmatrix} \quad (1)$$

$$\text{where, } m_1 = k_{PT} + k_C$$

$$m_2 = k_{rec} + k_{dis} + k_Z$$

$$m_3 = k_Z \text{ (since } k_q[H_3O^+] \text{ is extremely low)}$$

It is important to mention here that, equation (1) represents the tri-exponential time dependent functions (Table 1) for the three species $[\chi_i^*] = C^*$, ($Z^* \dots H_3O^+$), Z^* inside liquid crystalline systems, which follows the decay equation as:

$$[\chi_i^*] = a_1 e^{-\alpha_1 t} + a_2 e^{-\alpha_2 t} + a_3 e^{-\alpha_3 t} \quad (2)$$

Here the three reciprocal decay times ($\alpha_i = \frac{1}{\tau_i}$) can be representing by the roots of third order equation as:

$$\begin{bmatrix} \alpha - m_1 & k_{rec} & 0 \\ k_{PT} & \alpha - m_2 & 0 \\ 0 & k_{dis} & \alpha - m_3 \end{bmatrix} = 0 \quad (3)$$

For solve this equation we have simplified this equation in the irreversible proton escape conditions, where $k_q[\text{H}_3\text{O}^+]$ can be neglected with respect to k_z . The three solutions of equation (3) (denominated $\alpha_1, \alpha_2, \alpha_3$) in the limit of $k_q[\text{H}_3\text{O}^+]_w = 0$.

$$\alpha_{2,1} = \frac{m_1 + m_2 \pm \sqrt{(m_1 - m_2)^2 + 4 k_{rec} \cdot k_{PT}}}{2} \quad (4)$$

In addition, the ratio of the pre-exponential factor, $R = \frac{a_2}{a_1}$ is related to the kinetic constants by equation^{1, 2}

$$R = \frac{m_1 - \alpha_1}{\alpha_2 - m_1} \quad (5)$$

Now, the different rate constants, decay parameter and pre-exponential ratio are related with the following equations as:

$$m_1 = \frac{R\alpha_2 + \alpha_1}{R + 1} \quad (6)$$

$$m_2 = \alpha_2 + \alpha_1 - m_1 \quad (7)$$

$$k_{PT} = m_1 - k_C \sim m_1 \quad (8)$$

$$k_{rec} = \frac{m_1 m_2 - \alpha_1 \alpha_2}{k_{PT}} \quad (9)$$

$$k_{dis} = m_2 - k_Z - k_{rec} \quad (10)$$

In the equation (8) k_C is negligible compare to m_1 . Finally, using the lifetime decay components and the corresponding amplitudes, the explicit form of different rate constants of the elementary steps of kinetic scheme can be depicted as:

$$k_{PT} = \frac{\frac{1}{\tau_1} + \frac{1}{\tau_2} \left(\frac{a_2}{a_1}\right)}{1 + \frac{a_2}{a_1}} \quad (11)$$

$$k_{rec} = \frac{\frac{1}{\tau_1} \left(\frac{a_2}{a_1}\right) + \frac{1}{\tau_2}}{1 + \frac{a_2}{a_1}} - \frac{1}{k_{PT} \tau_1 \tau_2} \quad (12)$$

$$k_{dis} = \frac{\left(\frac{a_2}{a_1}\right) \frac{1}{\tau_1} + \frac{1}{\tau_2}}{1 + \frac{a_2}{a_1}} - \frac{1}{\tau_3} - k_{rec} \quad (13)$$

Here, τ_1 is the short life time component of the decay of C*-TPT form ($\lambda_{coll}= 420$ nm) with corresponding amplitude a_1 and τ_2 is the intermediate component of the decay of C*-TPT form ($\lambda_{coll}= 420$ nm) with the corresponding amplitude a_2 . τ_3 is the long lifetime component decay of Z* form ($\lambda_{coll}=570$ nm).

References:

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