Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

SUPPLEMENTARY INFORMATION

The Contributions of Molecular Vibrations and Higher Triplet Levels to the Intersystem Crossing Mechanism in Metal-Free Organic Emitters.

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Figure S1-(a) Steady-state emission spectra in solid ethanol solution at 100 K for compounds **1–10**. The compounds **1**, **3** and **5** show no phosphorescence, whereas their corresponding regioisomers show strong dual fluorescence-phosphorescence.

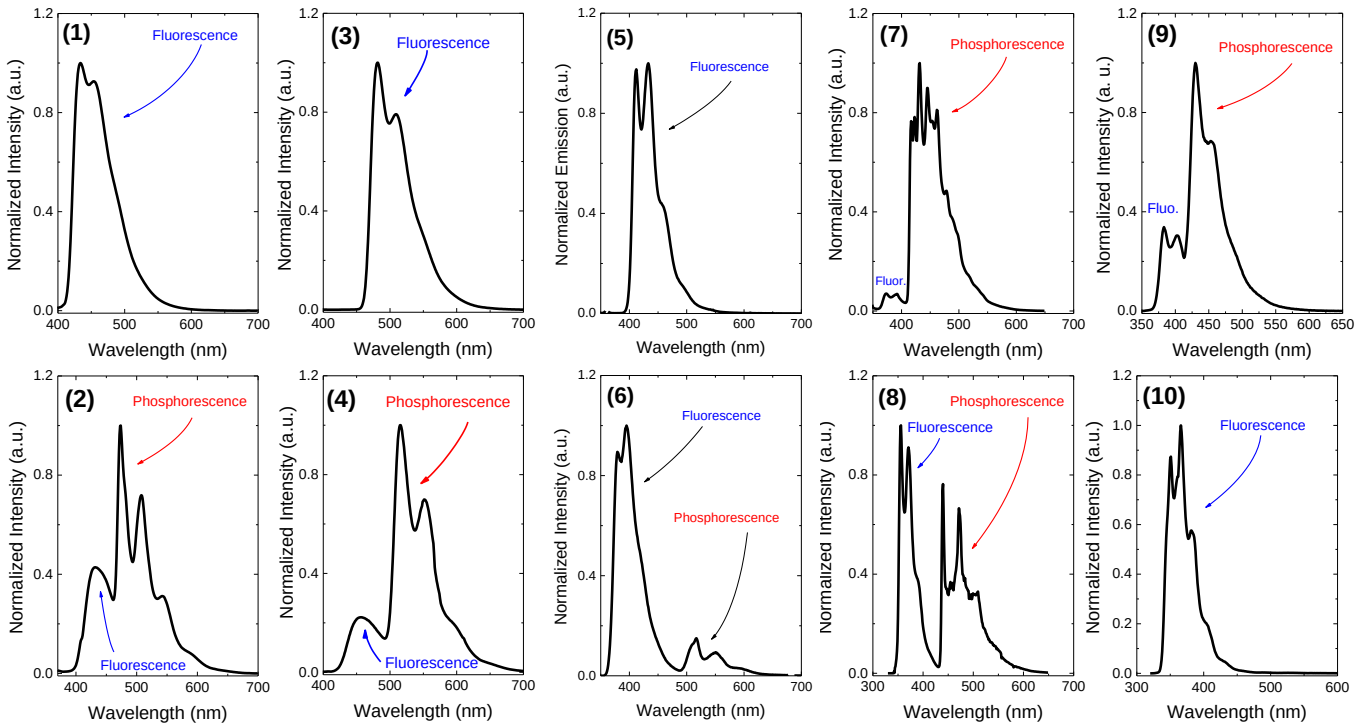


Figure S2- (a) Fluorescence decay showing prompt and delayed fluorescence components for compounds **3** and **4** in ethanol solution at 300 K. (b) Power dependence of the integrated delayed fluorescence in **3** and **4**. The slope in **3** is 2 whereas in **4** is 1, showing the different nature of the mechanisms that give origin to the delayed fluorescence, triplet-triplet annihilation (TTA) and TADF, respectively.

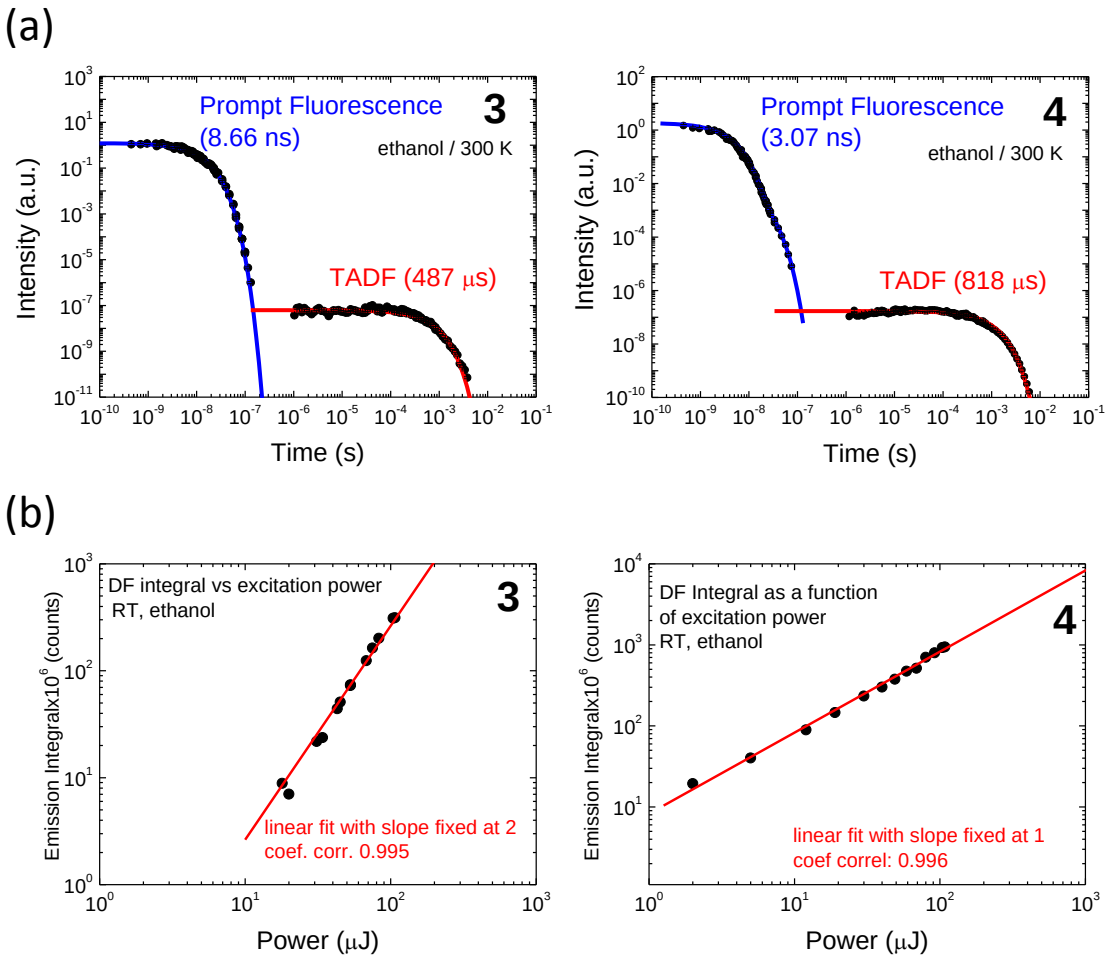


Figure S3- Steady-state emission in zeonex at 300 K in the presence of oxygen and in vacuum. Compounds **1**, **3**, and **5** show no phosphorescence at 300 K. However, their corresponding isomers show intense RTP. Compounds **7** and **8** are "angular" substituted and also show RTP. In **9**, instead of RTP, the increase of the fluorescence intensity upon degassing indicates the presence of TADF. Note that in all the compounds, with the exception of **9**, the intensity of the fluorescence band is practically not affected by presence/absence of oxygen.

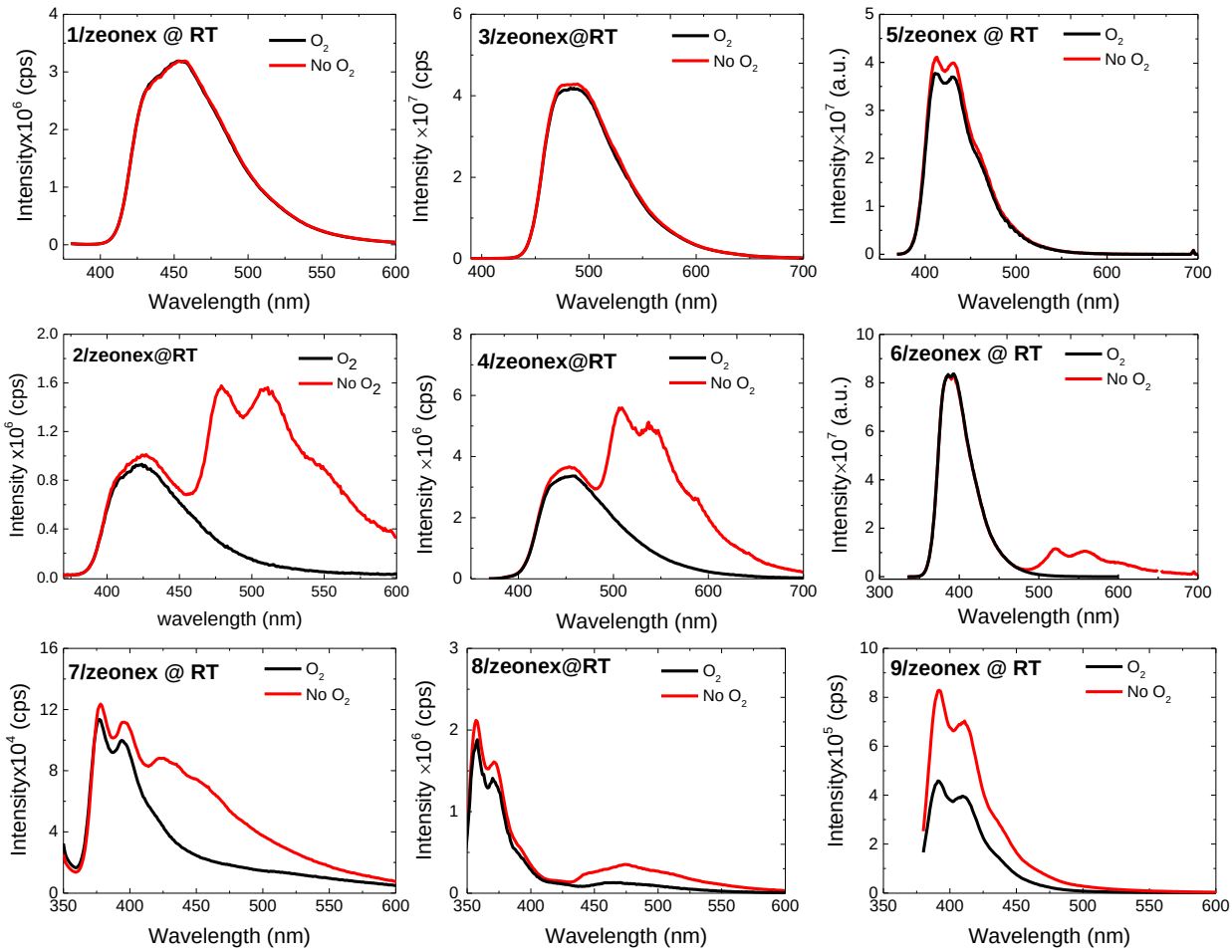


Figure S4- Fluorescence decays of compounds **1–4** in zeonex solid film at room temperature, collected at the fluorescence band.

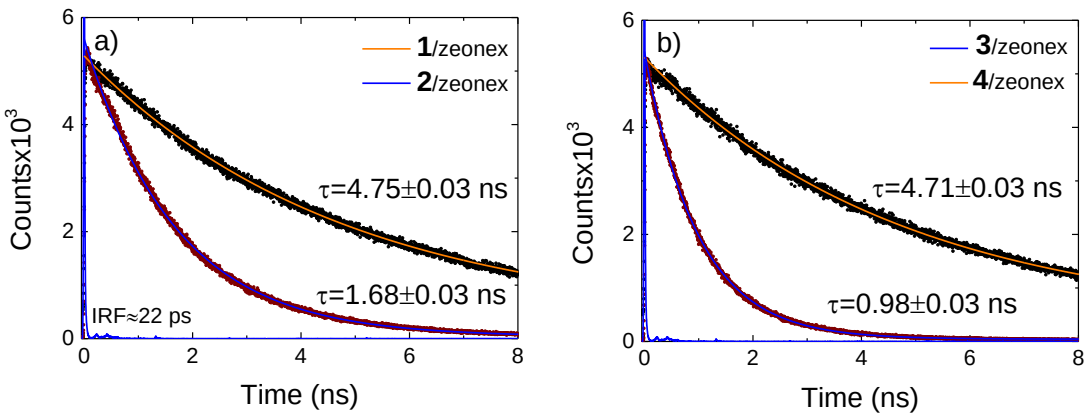


Figure S5- Fluorescence decays of compounds **2** and **4** in zeonex solid film at room temperature, collected at the phosphorescence band.

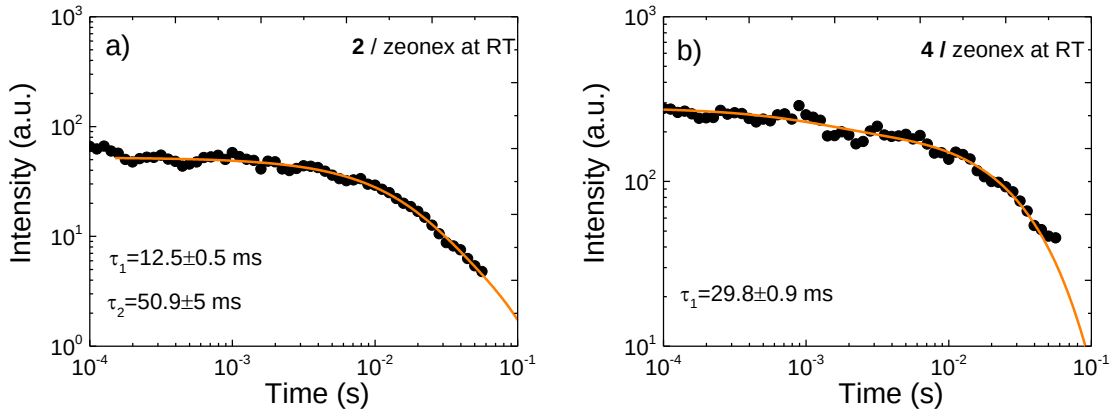


Figure S6-HOMO and LUMO contour plots for compounds **3–4**.

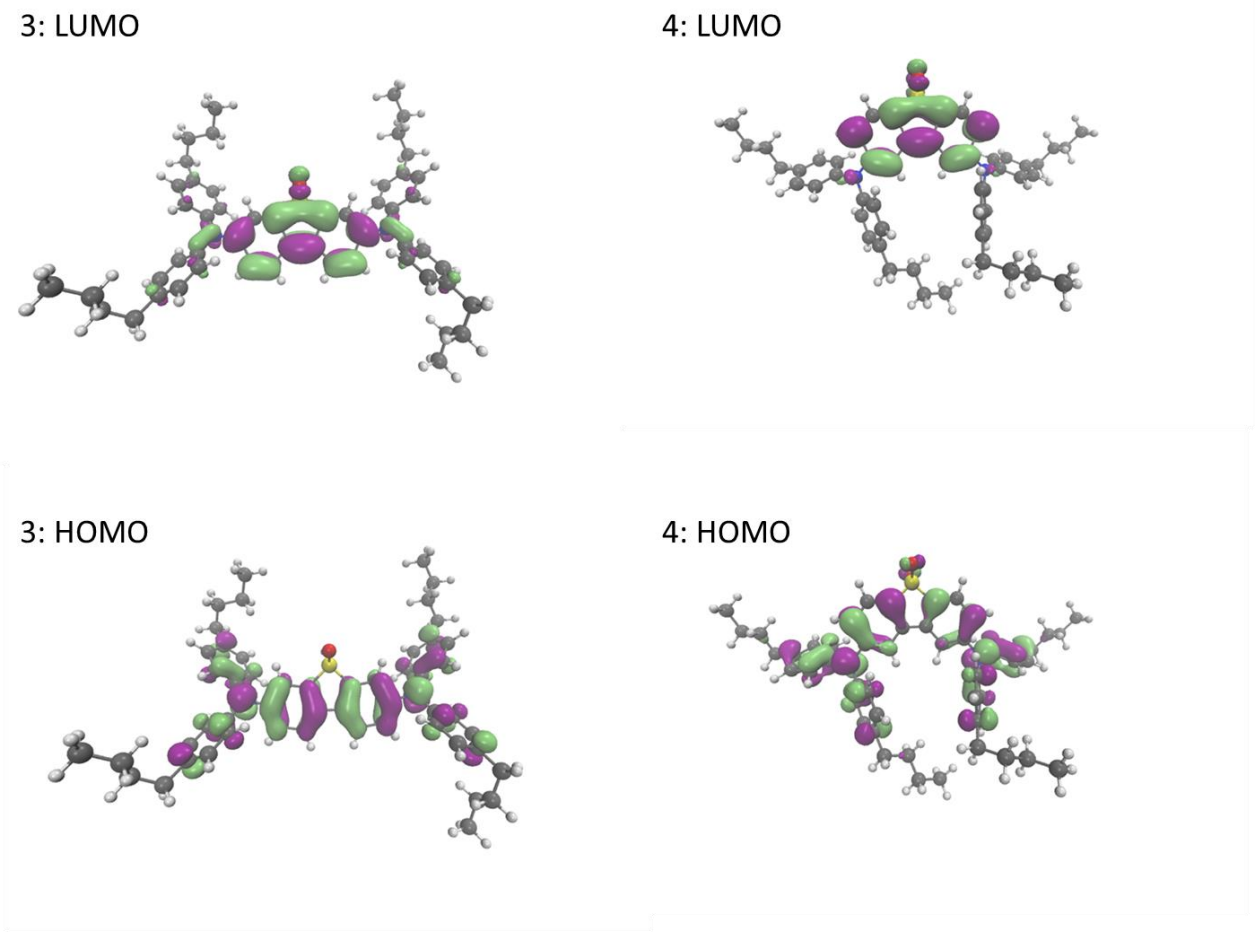


Figure S7- Molecular structures of hosts (a) TSPO1 and (b) poly(4-bromostyrene) (PBrS).

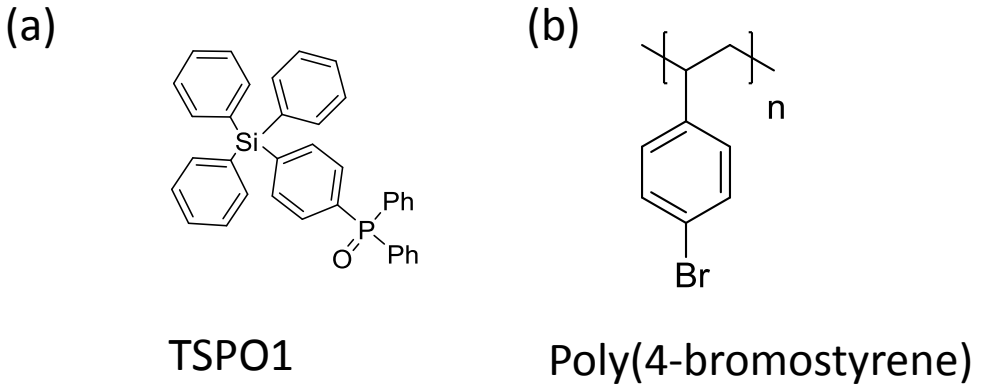


Figure S8- Steady-state emission spectra of compounds **1–4** dispersed in PBrS, in vacuum (red) and in air equilibrated (black) conditions at 300 K. Compounds **2** and **4** show dual luminescence, TADF and RTP, compounds **1** and **3** show only prompt fluorescence.

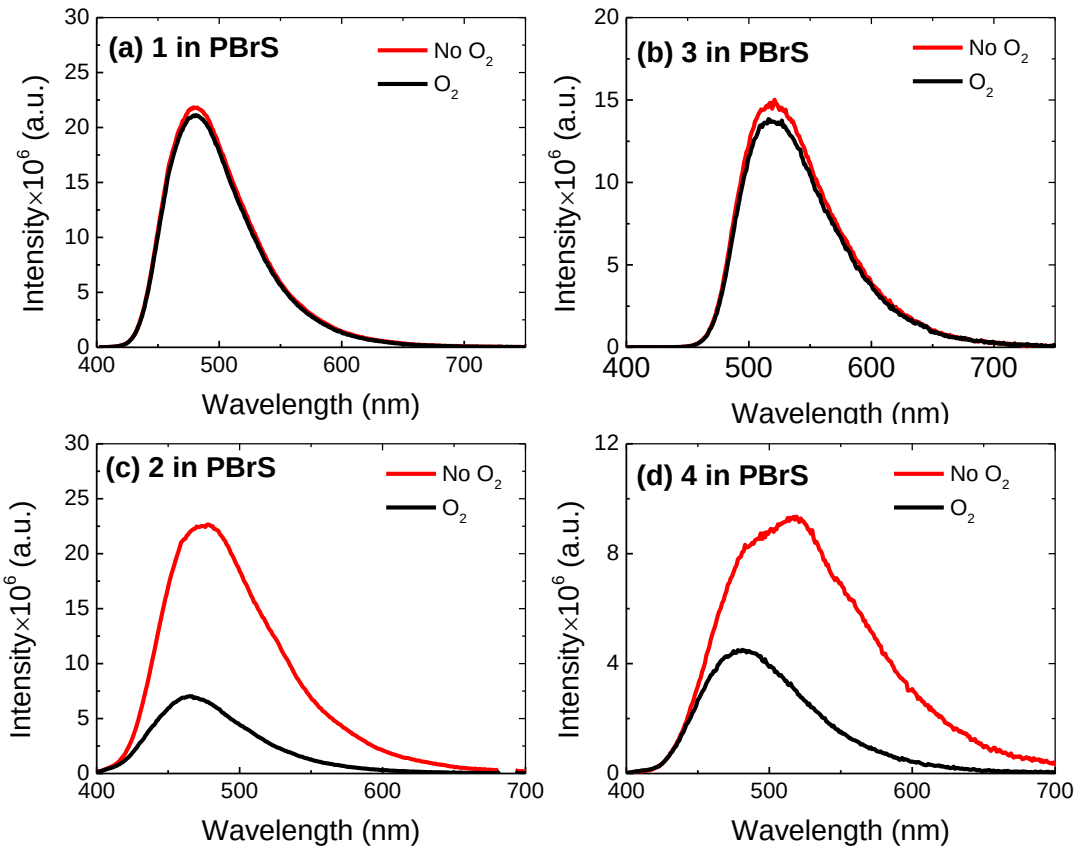


Figure S9- Steady-state emission spectra of compound **2** dispersed in different hosts (a) **7**, (b) **9**, (c) TSPO1 and (d) PBrS, in vacuum (red) and air equilibrated (black) conditions.

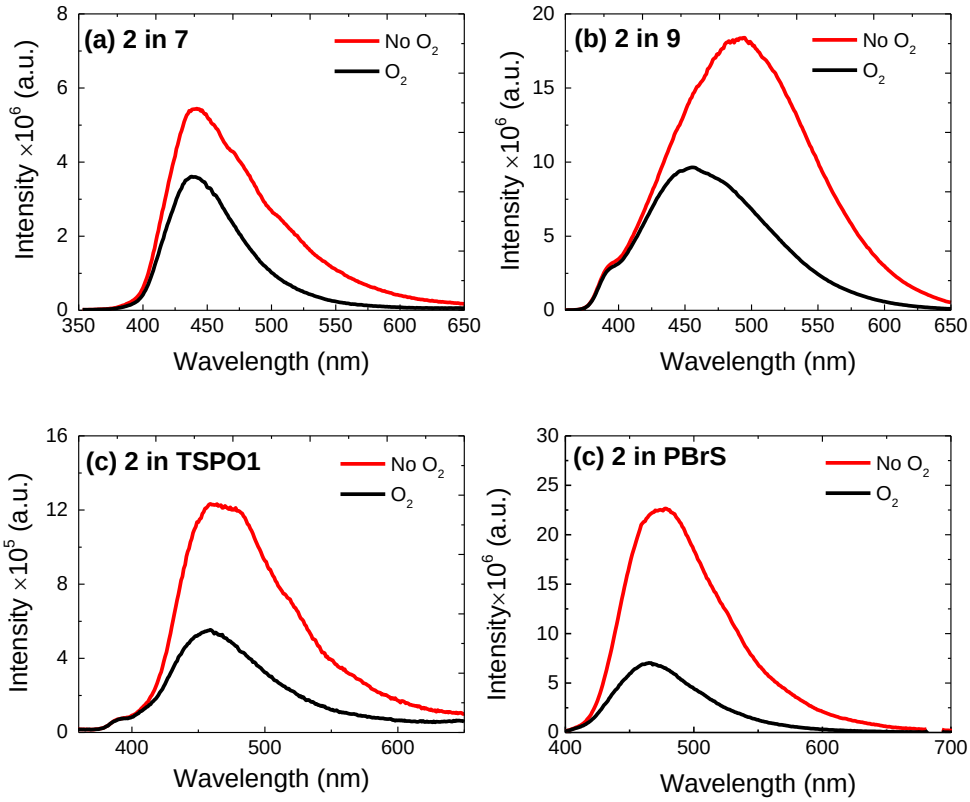


Figure S10- Time-resolved luminescence decays for compounds **2** and **4** dispersed in **7**, **9** and TSPO1 hosts. In all cases long-lived dual luminescence is observed.

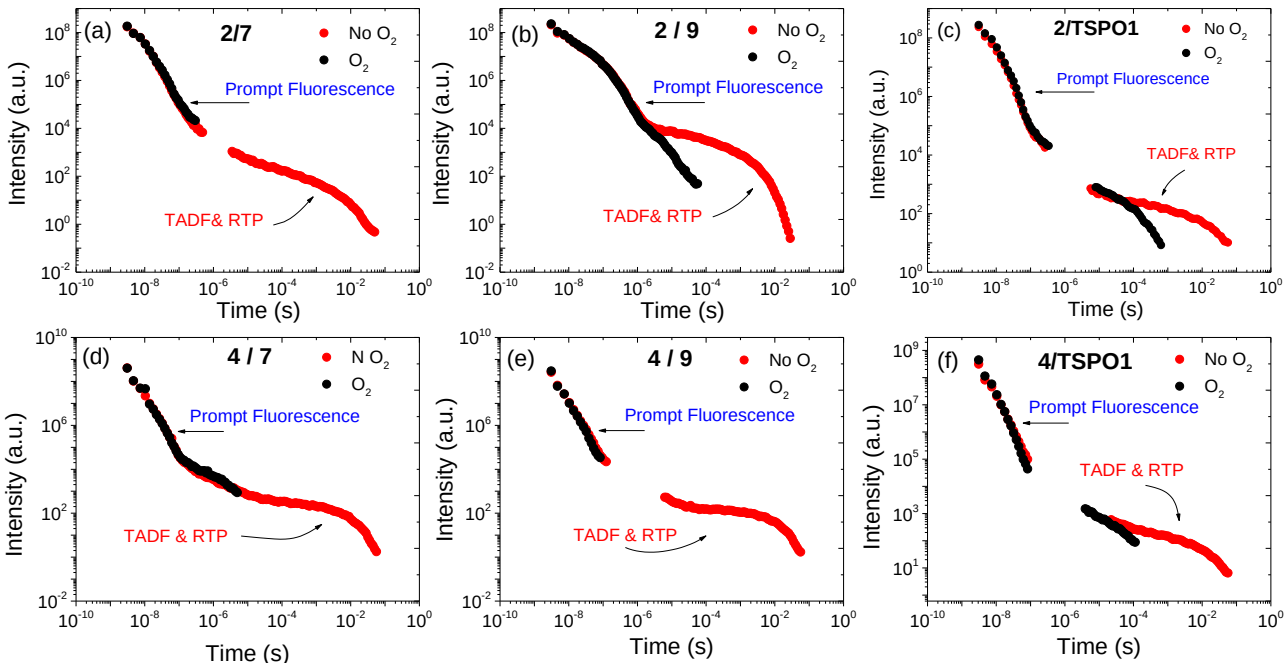


Figure S11-Time-resolved spectra of compounds **2 and 4** dispersed in **7**, **9** and TSPO1 showing the spectra of the prompt fluorescence (black), and long-lived TADF and RTP (red). Both spectra are compared with the steady-state emission spectra in zeonex (blue).

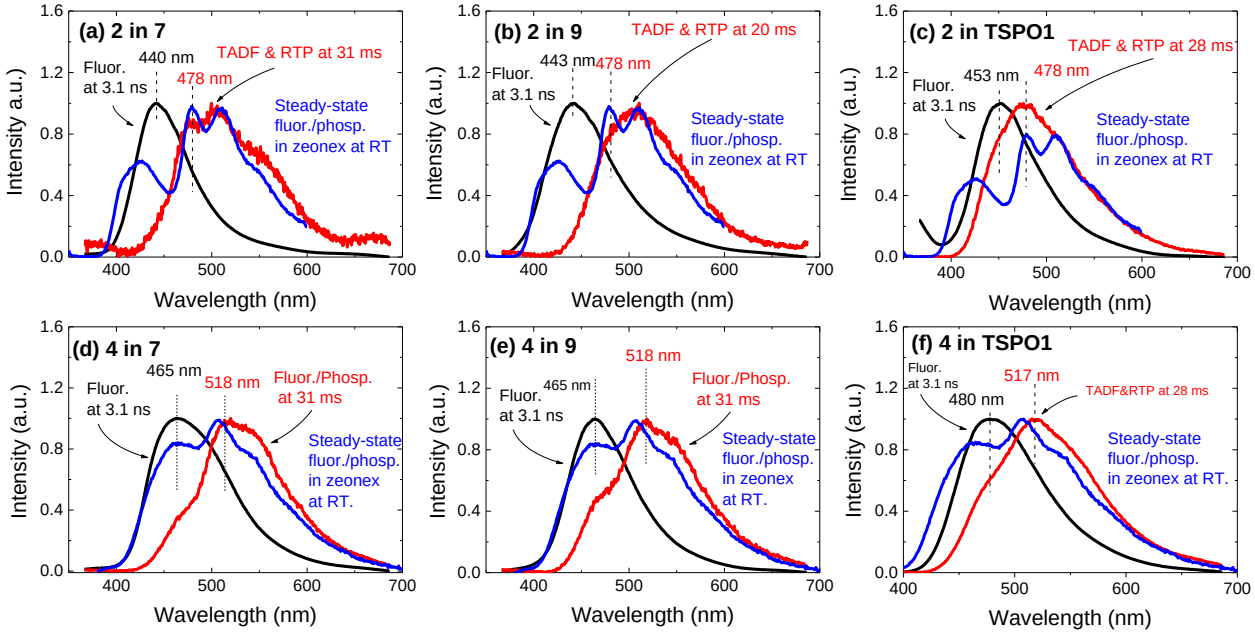


Figure S12- Triplet transient absorption decays for compounds **2, 4** and **6-9** in deaerated *n*-hexane upon excitation at 355 nm followed at absorption maxima with (red) and without (black) β-carotene

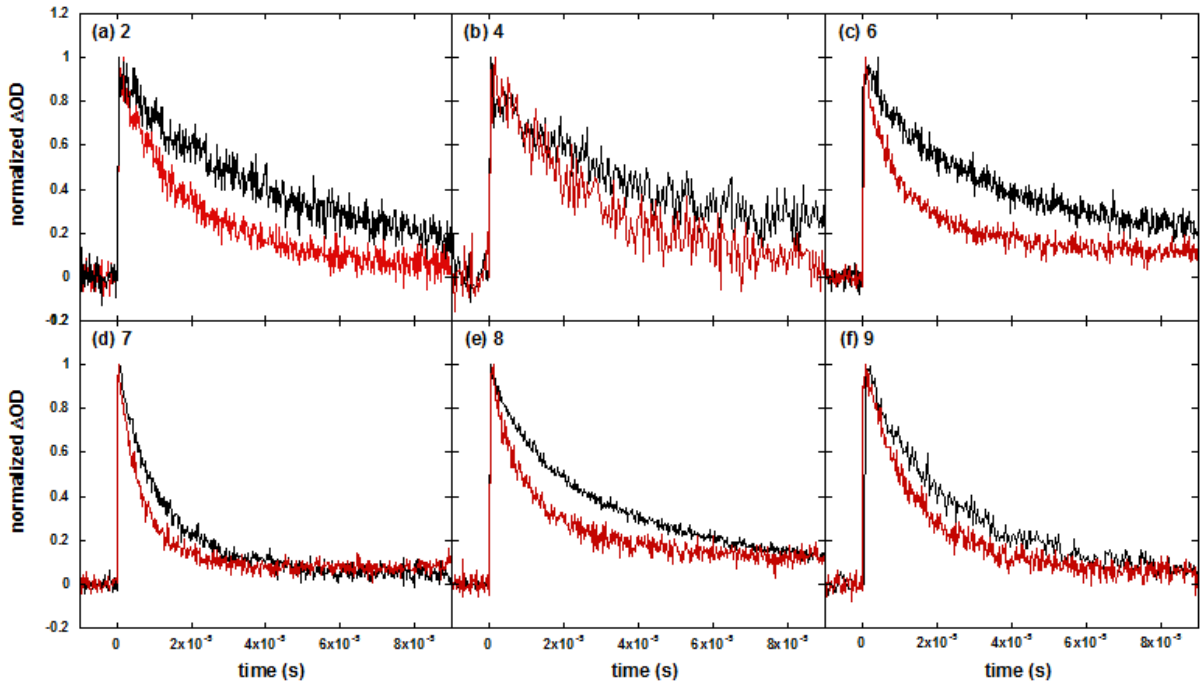


Figure S13- Triplet transient absorption spectra for compounds (a) **2,** (b) **4,** (c) **6,** (d) **7,** (e) **8** and (f) **9** in deaerated *n*-hexane with (red) and without (black) *β*-carotene as triplet quencher

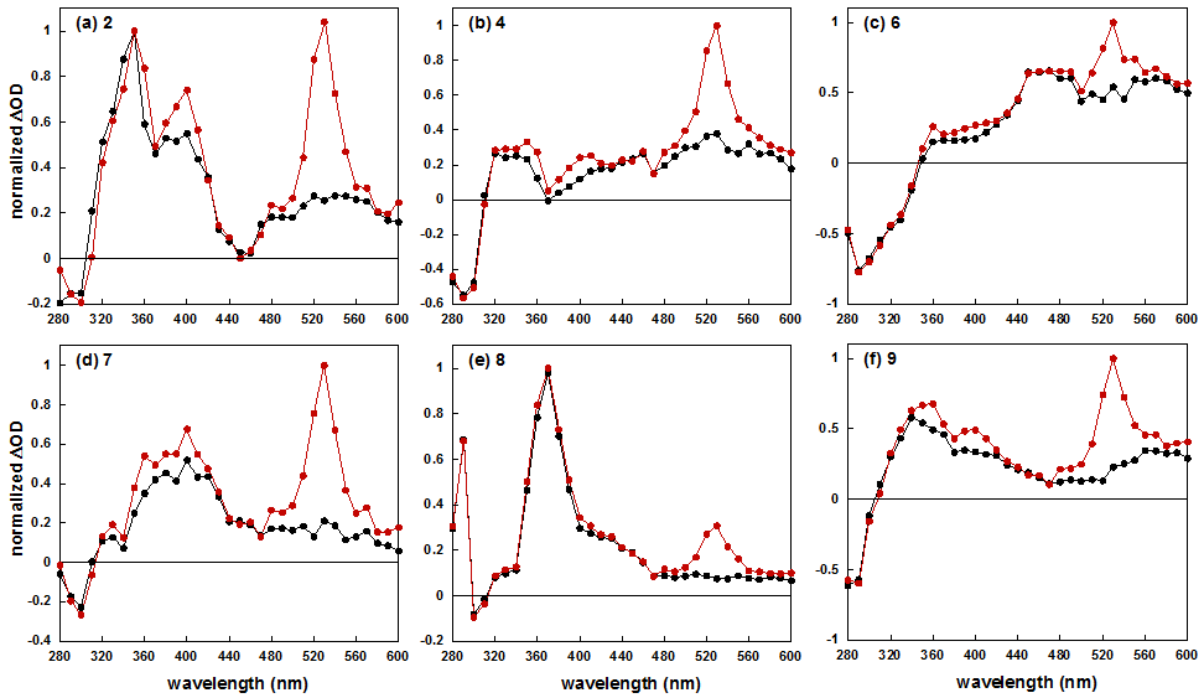
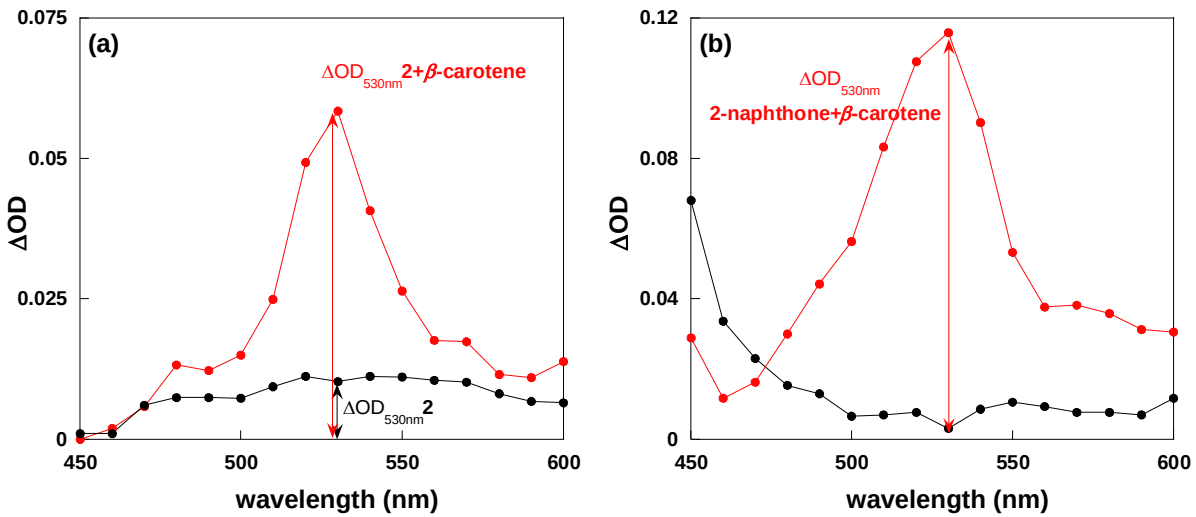


Figure S14 – Triplet transient absorption spectra for compound (a) **2** and (b) **2-napthone** evidencing the increase in ΔOD at 530 nm in the presence of β-carotene.



From the decays in Figure S12, the efficiency of energy transfer from the standard P_{ET} (N) and the studied compounds, P_{ET}, to β-carotene can be determined by measuring the triplet lifetime of the donor in the absence (τ_{T0}) and in the presence ($\tau_{T'}$) of β-carotene, as in equation S1

$$P_{ET} = \frac{\tau_T^0 - \tau_T^{'}}{\tau_T^0} \qquad \text{S1}$$

The change in absorbance at 530 nm in the transient spectra of Figure S13 allows the determination of the relative concentration of β-carotene triplet formed upon excitation of the studied compounds compared to the standard in the same conditions, as in equation S2.

$$[\beta - carotene]^{'} = \frac{\Delta OD_{(\beta-carotene)} - \Delta OD}{\Delta OD_{(2-Naphthone+\beta-carotene)}} \qquad \text{S2}$$

Thus, final ϕ_T values are obtained from equation S3

$$\phi_T = \phi_{T(2-naphthone)}[\beta - carotene]^{'} \frac{P_{ET(2-naphthone)}}{P_{ET}} \qquad \text{S3}$$