The dependence of the ratio I_{exp}/I_{tot} on the concentration of naphthalene under optical excitation can be calculated from the following expressions discussed in the main text:

$$I_{naph} = I_{naph}^{abs} \cdot \frac{\varphi_{naph} \cdot \tau_f^{-1}}{k_d[DMA] + \tau_f^{-1}} \qquad (Eq.1)$$

$$I_{DMA} = I_{DMA}^{abs} \cdot \varphi_{DMA} \qquad (Eq.2)$$

$$\varphi_{exp} = \frac{k_d[DMA]}{k_d[DMA] + \tau_f^{-1}} \qquad (Eq.3)$$

$$N_{exp} = I_{naph}^{abs} \cdot \varphi_{exp} \qquad (Eq.4)$$

$$I_{exp} = N_{exp} \cdot \gamma_e = I_{naph}^{abs} \cdot \frac{k_d[DMA]}{k_d[DMA] + \tau_f^{-1}} \cdot \gamma_e \qquad (Eq.5)$$

$$I_{naph}^{abs} = \frac{D_{naph}}{D_{naph} + D_{DMA}} I_{\Sigma}^{abs} \qquad (Eq.6)$$

Then we have:

$$\frac{I_{exp}}{I_{naph} + I_{DMA}} = \frac{I_{naph}^{abs} \cdot \frac{k_d[DMA]}{k_d[DMA] + \tau_f^{-1}} \cdot \gamma_e}{I_{naph}^{abs} \cdot \frac{\varphi_{naph} \cdot \tau_f^{-1}}{k_d[DMA] + \tau_f^{-1}} + I_{DMA}^{abs} \cdot \varphi_{DMA}} = \frac{I_{naph}^{abs} \cdot k_d[DMA] \cdot \gamma_e}{I_{naph}^{abs} \cdot \varphi_{naph} \cdot \tau_f^{-1} + I_{DMA}^{abs} \cdot \varphi_{DMA}(k_d[DMA] + \tau_f^{-1})} =$$

$$= \frac{D_{naph} \cdot k_d[DMA] \cdot \gamma_e}{D_{naph} \cdot \varphi_{naph} \cdot \tau_f^{-1} + D_{DMA} \cdot \varphi_{DMA}(k_d[DMA] + \tau_f^{-1})} = \frac{\varepsilon_{naph} \cdot [Naph] \cdot k_d[DMA] \cdot \gamma_e}{\varepsilon_{naph} \cdot [Naph] \cdot \varphi_{naph} \cdot \tau_f^{-1} + \varepsilon_{DMA} \cdot [DMA] \cdot \varphi_{DMA}(k_d[DMA] + \tau_f^{-1})}$$

where τ_f is the fluorescence decay time for naphthalene (96 ns), φ_{naph} is the emission quantum yield for naphthalene (0.23), k_d is diffusion-controlled rate constant in *n*-dodecane (8.4×10^9 M^{-1}·s^{-1}), φ_{DMA} is the emission quantum yield of DMA (0.11), ε_{naph} is molar extinction coefficient for naphthalene at 290 nm (3200 M^{-1}·cm^{-1}) and ε_{DMA} is molar extinction coefficient or DMA at 290 nm (2200 M^{-1}·cm^{-1})[53], [DMA] is fixed at 10^{-2} M, the range of naphthalene concentrations is $10^{-3} - 5 \times 10^{-3}$ M, and γ_e is the (unknown)luminescence quantum yield of exciplex. Substituting the numerical values, we have approximately:

$$\frac{I_{exp}}{I_{naph} + I_{DMA}} \approx \frac{3 \cdot 10^{11} \cdot [Naph] \cdot \gamma_e}{8 \cdot 10^9 \cdot [Naph] + 3 \cdot 10^8 M} \approx \frac{10^3 \cdot [Naph] \cdot \gamma_e}{30 \cdot [Naph] + 1 M} = F(naph) \cdot \gamma_e$$

Function *F(naph)* for the range of naphthalene concentrations used in this work is plotted below.
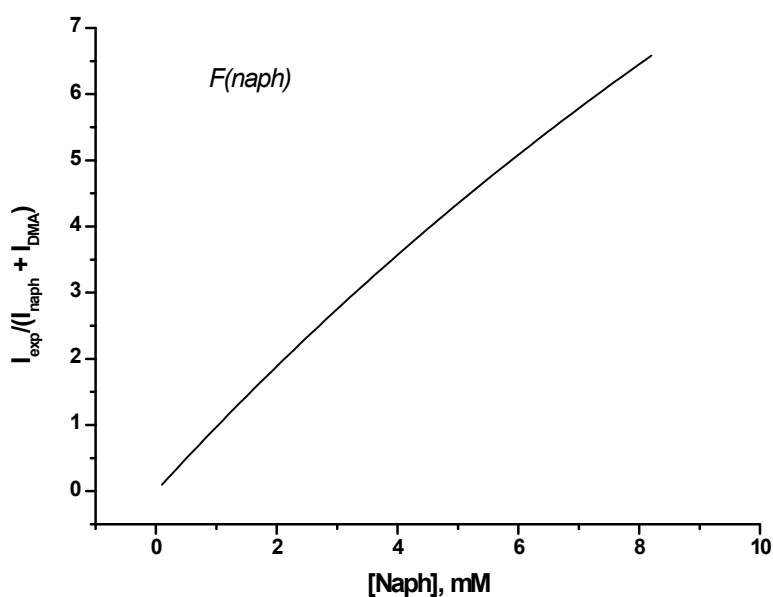
The formation of exciplexes from the excited DMA molecules in solutions of naphthalene and DMA can be neglected in the conditions of this work, as it is at least an order of magnitude less effective than the channel of excited naphthalene molecules. Similar to equations Eq.3 and Eq.4, we can write:

$$\varphi_{\exp,DMA} = \frac{k_d[Naph]}{k_d[Naph] + \tau_{f,DMA}^{-1}}$$

$$N_{\exp,DMA} = I_{DMA}^{abs} \cdot \varphi_{\exp,DMA} = I_{DMA}^{abs} \cdot \frac{k_d[Naph]}{k_d[Naph] + \tau_{f,DMA}^{-1}}$$

Then we have:

$$\frac{N_{\exp,naph}}{N_{\exp,DMA}} = \frac{I_{naph}^{abs}}{I_{DMA}^{abs}} \cdot \frac{\dfrac{k_d[DMA]}{k_d[DMA] + \tau_{f,naph}^{-1}}}{\dfrac{k_d[Naph]}{k_d[Naph] + \tau_{f,DMA}^{-1}}} = \frac{\varepsilon_{naph} \cdot [Naph]}{\varepsilon_{DMA} \cdot [DMA]} \cdot \frac{[DMA] \cdot (k_d[Naph] + \tau_{f,DMA}^{-1})}{[Naph] \cdot (k_d[DMA] + \tau_{f,naph}^{-1})}$$

where $\tau_{f,naph}$ is the fluorescence decay time for naphthalene (96 ns), $\tau_{f,DMA}$ is the fluorescence decay time for DMA (2.4 ns), k_d is diffusion-controlled rate constant in n-dodecane (8.4×10^9 $M^{-1} \cdot s^{-1}$), ε_{naph} is molar extinction coefficient for naphthalene at 290 nm (3200 $M^{-1} \cdot cm^{-1}$) and ε_{DMA} is molar extinction coefficient or DMA at 290 nm (2200 $M^{-1} \cdot cm^{-1}$)[53], [DMA] is fixed at 10^{-2} M.

Taking the highest used concentration of naphthalene (5×10^{-3} M), we have:

$$\frac{N_{\exp,naph}}{N_{\exp,DMA}} \approx \frac{3200}{2200} \cdot \frac{5 \cdot 10^8}{9 \cdot 10^7} \approx 8$$

Thus in our experimental conditions the exciplexes formed by the reaction between the excited DMA molecules and the ground-state naphthalene molecules can be neglected relative to the exciplexes formed by the reaction between the excited naphthalene molecules and the ground-state DMA molecules.