Electronic Supplementary Information

Photocatalytic Mechanism of Organic Dithienophosphole Derivatives as Highly Efficient Photo-redox Catalysts

Ping-Ping Sun,[a] Weijie Chi,[b] Devesh R. Kripalani,[a] Kun Zhou[a,c]*

[a] *Singapore Centre for 3D Printing, School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*

[b] *Science, Mathematics and Technology Cluster, Singapore University of Technology and Design, 8 Somapah Road, Singapore 487372, Singapore*

[c] *Environmental Process Modelling Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 CleanTech Loop, Singapore 637141, Singapore*

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Note S1. Kinetic Analysis of the Activation Mechanism by Modified Marcus Theory

In order to obtain further insights into the mechanisms of the activation processes, the investigation on electron transfer (ET) kinetics is of great importance. Marcus theory has been well-known for describing ET processes,[1] although this theory cannot be simply used for the current assessment of ET kinetics because a concerted dissociative electron transfer (DET) to Ar_2I^+/EDB is involved in the reaction process.[2-6] However, a modified model of Marcus theory, proposed by Savéant,[7-9] is accessible and has already been used to analyze the dynamics of DET processes successfully.[3-5, 10, 11] Besides, inner- and outer-sphere electron transfer (ISET and OSET) mechanisms have also been analyzed by using such modified Marcus theory.[1, 7]

Note S1.1 Act-1 PC–Ar_2I^+ activation process

The reduction of Ar_2I^+ and activation of PCs (Ph-DTP and TPA-DTP) undergo the following reaction paths (S1, S2), where an outer-sphere electron transfer (OSET) occurs from the donor (PC*) to the acceptor (Ar_2I^+) by breaking the concerted C-I bond in Ar_2I^+. This process is also known as DET.

$$\mathrm{PC} \rightarrow \mathrm{PC^*} \tag{S1}$$

$$\mathrm{PC^*} + \mathrm{Ar_2I^+} \rightarrow \mathrm{PC^{\bullet+}} + \mathrm{Ar_2I^\bullet} \rightarrow \mathrm{PC^{\bullet+}} + \mathrm{Ar^\bullet} + \mathrm{ArI} \tag{S2}$$

According to the sticky model of DET theory,[4, 7, 8, 10] the rate constant k_{act} of the Act-1 activation process can be calculated via the following equations.

$$k_{\mathrm{act}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{S3}$$

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}} G^{\theta} - D_{\mathrm{P}}}{4\Delta G_0^{\ddagger}}\right)^2 \tag{S4}$$

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + \left(\sqrt{D_{\mathrm{B}}} - \sqrt{D_{\mathrm{P}}}\right)^2}{4} \tag{S5}$$

$$\Delta_{\mathrm{r}} G^{\theta} = F\left(E^{\theta}_{\mathrm{PC^{\bullet+}/PC^*}} - E^{\theta}_{\mathrm{Ar_2I^+/Ar_2I^\bullet}}\right) - \frac{N_{\mathrm{A}} e^2}{4\pi\varepsilon_0 \varepsilon r} \tag{S6}$$

$$E^{\theta}_{\mathrm{PC}^{\bullet+}/\mathrm{PC}*} = E^{\theta}_{\mathrm{PC}^{\bullet+}/\mathrm{PC}} - E_{h\upsilon} = E^{\theta}_{\mathrm{PC}^{\bullet+}/\mathrm{PC}} - \frac{hc}{\lambda_{\mathrm{max}}} \tag{S7}$$

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\,(r_{\mathrm{PC}*} + r_{\mathrm{Ar_2I^+}})^2 \tag{S8}$$

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{PC}*}} + \frac{1}{2r_{\mathrm{eff}}} - \frac{1}{r_{\mathrm{PC}*}+r_{\mathrm{eff}}}\right) \tag{S9}$$

$$\varphi_{\mathrm{act}} = k_{\mathrm{act}}[\mathrm{Ar_2I^+}]\tau_0\Phi_{\mathrm{F}} \tag{S10}$$

In the above equations, PC refers to the photo-redox catalyst used in this work, namely, the DTP derivatives (TPA-DTP and Ph-DTP). In eq S3, $\Delta G^{\ddagger}$ is the activation free energy, and can be considered as the activation barrier of the reaction. Z is the pre-exponential factor, and can be calculated by eq S8, in which, N_{A} is the Avogadro constant, μ is the reduced mass, R is the gas constant and T is the temperature. Both $r_{\mathrm{PC}*}$ and $r_{\mathrm{Ar_2I^+}}$ are the radii of the respective molecules obtained from the computed volume of the molecules shown in Table S1, which are based on an isoelectronic density surface of 0.001 electrons/Bohr^3 by using the DFT optimized structures. $\Delta G_0^{\ddagger}$ is the intrinsic barrier of the reaction, which is the activation free energy when $\Delta_{\mathrm{r}}G^{\theta} = 0$ and can be calculated by eq S5. In eq S5, D_{B} is the bond dissociation energy of $\mathrm{Ar_2I^{\bullet}}$, obtained from DFT calculations. D_{p} is the interaction energy produced between ion-dipole adducts. λ_0 is the solvent reorganization energy and can be determined by using an empirical equation as shown in eq S9,[12, 13] where r_{eff} is the effective radius of $\mathrm{Ar_2I^+}$, defined as $r_{\mathrm{eff}} = (2r_{\mathrm{Ar_2I^+}} - r_{\mathrm{ArI}})r_{\mathrm{ArI}}/r_{\mathrm{Ar_2I^+}}$.

$\Delta_{\mathrm{r}}G^{\theta}$ in eq S4 refers to the reaction free energy. $\Delta_{\mathrm{r}}G^{\theta}$ of reaction S2 can be calculated from the standard potentials of the electron donor ($\mathrm{PC^{\bullet+}/PC*}$) and acceptor ($\mathrm{Ar_2I^+/Ar^{\bullet} + ArI}$) redox couples, $E^{\theta}_{\mathrm{PC}^{\bullet+}/\mathrm{PC}*}$ and $E^{\theta}_{\mathrm{Ar_2I^+/Ar^{\bullet}+ArI}}$, as shown in eq S6.[14] In this equation, $E^{\theta}_{\mathrm{Ar_2I^+/Ar^{\bullet}+ArI}}$ is the standard reduction potential in the ground state, while $E^{\theta}_{\mathrm{PC}^{\bullet+}/\mathrm{PC}*}$ is the standard oxidation potential in the excited state and can be obtained from eq S7 by considering the relationship between the standard oxidation potential of the donor $\mathrm{PC^{\bullet+}}$ in the ground state and the excitation energy of the excited reactant E_{hv}. E_{hv} equals to $hc/\lambda_{\mathrm{max}}$, where h is the Planck constant, c is the speed of light, and λ_{max} is the wavelength of maximum emission intensity of the excited state. In eq S6, e is the elementary charge, ε_0 is the permittivity of vacuum, and ε is the relative permittivity of the solvent at room temperature. The last term is the Columbic energy experienced by the radical ion pair at a distance r, where r is approximately the sum of the radii of two hitting molecules $r = r_{\mathrm{PC}*} + r_{\mathrm{Ar_2I^+}}$.

The activation of PC* has to compete with all decay pathways (radiative and nonradiative) that can bring themselves back to their ground state. The quantum yield for the reaction from a given excited state can be calculated by eq S10, whereby Φ_{F} is the fluorescence quantum efficiency for the generation of the excited state, τ_0 is the lifetime of the excited state, and $[\mathrm{Ar_2I^+}]$ is the concentration, which is considered to be roughly constant during the reaction.

Table S1. Geometric, thermodynamic and kinetic parameters in the activation processes.

Donor	Acceptor	r_{donor}[a] /Å	r_{acceptor}[b] /Å	r_{eff} /Å	λ_0 /kcal mol^{-1}	D_{B} /kcal mol^{-1}	D_{P} /kcal mol^{-1}
Ph-TPA*	$\mathrm{Ar_2I^+}$	9.54	8.04	7.371	5.81	2.75	0.86
TPA-DTP*	$\mathrm{Ar_2I^+}$	14.02	8.04	7.371	5.39	2.75	0.86
Ph-TPA*	ArI	9.54	5.72	3.275	12.07	35.06	1.34
TPA-DTP*	ArI	14.02	5.72	3.275	12.4	35.06	1.34
EDB	Ph-TPA*	6.91	9.54	—	6.08	177.08[c]	—
EDB	TPA-DTP*	6.91	14.02	—	5.73	177.08[c]	—

[a] donor radius, [b] acceptor radius, [c] bond dissociation energy of $\mathrm{EDB^{\bullet+}} \rightarrow \mathrm{EDB^{\bullet}(–H)} + \mathrm{H^+}$,

With the calculated maximum emission wavelength of both DTPs (Fig. 1), their standard oxidation potential can be obtained from eq S7, where

$E^{\theta}_{\mathrm{PC^{\bullet+}/PC*}}$ (Ph-DTP) = $E^{\theta}_{\mathrm{PC^{\bullet+}/PC}}$ (Ph-DTP) – $E_{h\upsilon}$ = 1.13 V – (6.63 × 10^{-34} J s × 3 ×10^{8} m/s)/(559 nm × 1.602 ×10^{-19} C) = – 1.09 V vs. SCE

$E^{\theta}_{\mathrm{PC^{\bullet+}/PC*}}$ (TPA-DTP) = $E^{\theta}_{\mathrm{PC^{\bullet+}/PC}}$ (TPA-DTP) – $E_{h\upsilon}$ = 0.79 V – (6.63 × 10^{-34} J s × 3 ×10^{8} m/s)/(615 nm × 1.602 ×10^{-19} C) = – 1.23 V vs. SCE

Since the reduction potential of $\mathrm{Ar_2I^+}$ is –0.73 V vs SCE[15] in acetonitrile (MeCN), the reaction free energy under each PC activation process can then be obtained by eq S6, where

$\Delta_{\mathrm{r}}G^{\theta}$ (Ph-DTP) = 96485 C mol^{-1} (–1.09 + 0.73) V – 6.022 × 10^{23} mol^{-1} × (1.602 × 10^{-19} C)^{2}/(4 ×

$3.14 \times 8.854 \times 10^{-12}$ $J^{-1}C^2m^{-1} \times 37.5 \times (9.542 + 8.038) \times 10^{-10}$ m) = –36.842 kJ mol^{-1} = – 8.8 kcal mol^{-1}

$\Delta_r G^\theta$ (TPA-DTP) = 96485 C mol^{-1} (–1.23 + 0.73) V – 6.022×10^{23} mol^{-1} × $(1.602 \times 10^{-19}$ C$)^2$/(4 × $3.14 \times 8.854 \times 10^{-12}$ $J^{-1}C^2m^{-1} \times 37.5 \times (14.017 + 8.038) \times 10^{-10}$ m) = –49.92 kJ mol^{-1} = –11.93 kcal mol^{-1}

With the obtained geometric parameters (Table S1), the solvent reorganization energy can be calculated by eq S9,

$$\lambda_0 \text{ (Ph-DTP)} = 95\left(\frac{1}{2r_{\mathrm{PC}*}} + \frac{1}{2r_{\mathrm{eff}}} - \frac{1}{r_{\mathrm{PC}*}+r_{\mathrm{eff}}}\right)$$

= 95[1/(2×9.542 Å) + 1/(2×7.371 Å) – 1/(9.542 Å + 7.371 Å)] = 5.81 kcal/mol

$$\lambda_0 \text{ (TPA-DTP)} = 95\left(\frac{1}{2r_{\mathrm{PC}*}} + \frac{1}{2r_{\mathrm{eff}}} - \frac{1}{r_{\mathrm{PC}*}+r_{\mathrm{eff}}}\right)$$

= 95[1/(2×14.017 Å) + 1/(2×7.371 Å) – 1/(14.017 Å + 7.371 Å)] = 5.39 kcal/mol

With the calculated D_B and D_p (Table S1), the intrinsic barrier $\Delta G_0^\ddagger$ and the activation free energy $\Delta G^\ddagger$ in each Act-1 activation process can be obtained by eqs S5 and S4, where

$\Delta G_0^\ddagger$ (Ph-DTP) = (5.81 kcal/mol +((2.75 kcal/mol)$^{1/2}$ – (0.86 kcal/mol)$^{1/2}$)^2)/4 = 1.586 kcal/mol

$\Delta G_0^\ddagger$ (TPA-DTP) = (5.39 kcal/mol +((2.75 kcal/mol)$^{1/2}$ – (0.86 kcal/mol)$^{1/2}$)^2)/4 = 1.481 kcal/mol

$\Delta G^\ddagger$ (Ph-DTP) = 1.586 kcal mol^{-1} × (1+(– 8.8 kcal mol^{-1} – 0.86 kcal mol^{-1})/(4×1.586 kcal mol^{-1}))^2 = 0.433 kcal mol^{-1}

$\Delta G^\ddagger$ (TPA-DTP) = 1.481 kcal mol^{-1} × (1+(– 11.93 kcal mol^{-1} – 0.86 kcal mol^{-1})/(4×1.481 kcal mol^{-1}))^2 = 1.989 kcal mol^{-1}

To obtain the rate constant k_{act} of the Act-1 activation process, the pre-exponential factor Z should first be calculated by eq S8, in which μ can be obtained by

$$\mu = \frac{M_{\mathrm{DTP}}M_{\mathrm{Ar_2I^+}}}{M_{\mathrm{DTP}}+M_{\mathrm{Ar_2I^+}}}$$

μ (Ph-DTP) = 440 g mol^{-1} × 393 g mol^{-1}/(440 g mol^{-1} + 393 g mol^{-1}) = 207.59 g mol^{-1}

μ (TPA-DTP) = 774 g mol^{-1} × 393 g mol^{-1}/(774 g mol^{-1} + 393 g mol^{-1}) = 260.65 g mol^{-1}

$$Z\,(\text{Ph-DTP}) = N_{\text{A}}\sqrt{\frac{8\pi RT}{\mu}}\left(r_{\text{Ph-DTP*}} + r_{\text{Ar}_2\text{I}^+}\right)^2$$

$= 6.022 \times 10^{23}\ \text{mol}^{-1} \times (8 \times 3.14 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 298.15\ \text{K} / 207.59\ \text{g mol}^{-1})^{1/2} \times (17.58\ \text{Å})^2$

$= 1.02 \times 10^{9}\ \text{mol}^{-1}\text{s}^{-1}\text{m}^{3} = 1.02 \times 10^{12}\ \text{M}^{-1}\text{s}^{-1}$

$$Z\,(\text{TPA-DTP}) = N_{\text{A}}\sqrt{\frac{8\pi RT}{\mu}}\left(r_{\text{TPA-DTP*}} + r_{\text{Ar}_2\text{I}^+}\right)^2$$

$= 6.022 \times 10^{23}\ \text{mol}^{-1} \times (8 \times 3.14 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 298.15\ \text{K} / 260.65\ \text{g mol}^{-1})^{1/2} \times (22.055\ \text{Å})^2$

$= 1.43 \times 10^{9}\ \text{mol}^{-1}\text{s}^{-1}\text{m}^{3} = 1.43 \times 10^{12}\ \text{M}^{-1}\text{s}^{-1}$

With the obtained Z and $\Delta G^{\ddagger}$, the rate constant k_{act} of each Act-1 activation process can be obtained by eq S3, where

k_{act} (Ph-DTP) = $1.02 \times 10^{12}\ \text{M}^{-1}\text{s}^{-1} \times \exp(-0.433\ \text{kcal mol}^{-1}/(8.314\ \text{Jmol}^{-1}\text{K}^{-1} \times 298.15\ \text{K})) = 4.91 \times 10^{11}\ \text{M}^{-1}\text{s}^{-1}$

k_{act} (TPA-DTP) = $1.43 \times 10^{12}\ \text{M}^{-1}\text{s}^{-1} \times \exp(-1.989\ \text{kcal mol}^{-1}/(8.314\ \text{Jmol}^{-1}\text{K}^{-1} \times 298.15\ \text{K})) = 4.97 \times 10^{10}\ \text{M}^{-1}\text{s}^{-1}$

The calculated lifetimes of the excited state of Ph-DTP and TPA-DTP are 4.41 ns and 3.57 ns, respectively. Combining the experimental concentration of Ar_2I^+ (0.0184 M) and the roughly determined Φ_{F} (on average 0.01), the quantum yield for the Act-1 reactions can be obtained by eq S10, where

φ_{act} (Ph-DTP) = $4.91 \times 10^{11}\ \text{M}^{-1}\text{s}^{-1} \times 0.0184\ \text{M} \times 4.41 \times 10^{-9}\ \text{s} \times 0.01 = 0.4$

φ_{act} (TPA-DTP) = $4.97 \times 10^{10}\ \text{M}^{-1}\text{s}^{-1} \times 0.0184\ \text{M} \times 3.57 \times 10^{-9}\ \text{s} \times 0.01 = 3.27 \times 10^{-2}$

Note S1.2 Standard reduction potential calculation of ArI $E^{0}_{\text{ArI/Ar}^{\bullet}\text{+I}^{-}}$

The reduction of ArI, similar with that of Ar_2I^+, yields I^- and $\text{Ar}^{\bullet}$ in one step and can formally be expressed as the sum of the homolytic dissociation of a C-I bond and one-electron reduction of the resulting radical, $\text{I}^{\bullet}$ to I^- (note that the reduction of Ar_2I^+ yields ArI and $\text{Ar}^{\bullet}$ in one step following a one-electron reduction of the resulting radical cation). Thus, the standard potential[15] for the overall reaction can be calculated as:

$$E^{\theta}_{\mathrm{ArI/Ar}^{\bullet}+\mathrm{I}^{-}} = -(\mathrm{BDE}_{\mathrm{gas}}+\Delta\Delta G^{\theta}_{0\to 298\mathrm{K.gas}}+\Delta G_{1\mathrm{atm}\to 1\mathrm{M}}+\Delta\Delta G^{\theta}_{\mathrm{solv}})/F+E^{\theta}_{\mathrm{I}^{\bullet}/\mathrm{I}^{-}}$$

where $\mathrm{BDE}_{\mathrm{gas}}$ is the (zero-point corrected) C-I bond homolytic dissociation energy in ArI, the $\Delta\Delta G^{\theta}_{0\to 298\mathrm{K.gas}}$ term is a contribution to the Gibbs energy of heating from 0 to 298 K, $\Delta G_{1\mathrm{atm}\to 1\mathrm{M}}$ is a correction for the standard state change from 1 atm to 1 mol L^{-1} (1.89 kcal mol^{-1} at 298 K), and $\Delta\Delta G^{\theta}_{\mathrm{solv}}$ is the difference between the solvation free energies of $\mathrm{Ar}^{\bullet}$ and $\mathrm{I}^{\bullet}$, and ArI. The redox potential for the $\mathrm{I}^{\bullet}/\mathrm{I}^{-}$ couple is calculated as:

$$E^{\theta}_{\mathrm{I}^{\bullet}/\mathrm{I}^{-}} = -(-\mathrm{EA}_{\mathrm{gas}}+\Delta\Delta G^{\theta}_{0\to 298\mathrm{K.gas}}+\Delta\Delta G^{\theta}_{\mathrm{solv}})/F$$

where $\mathrm{EA}_{\mathrm{gas}}$ is the adiabatic electron affinity of $\mathrm{I}^{\bullet}$ (i.e., the negative of the enthalpy change at 0 K for the reduction), and $\Delta\Delta \mathrm{G}^{\theta}_{\mathrm{solv}}$ equals to the difference: $\Delta\Delta \mathrm{G}^{\theta}_{\mathrm{solv}}(\mathrm{I}^{\bullet}) - \Delta\Delta \mathrm{G}^{\theta}_{\mathrm{solv}}(\mathrm{I}^{-})$.

The reference values of $\mathrm{BDE}_{\mathrm{gas}}$ (55 kcal mol^{-1}) and $\mathrm{EA}_{\mathrm{gas}}$ (2.81 eV vs. experimental 3.057 eV) are taken from M062X/def2SVP calculations. The calculated thermal correction is –1.67 kcal/mol and $\Delta\Delta \mathrm{G}^{\theta}_{\mathrm{solv}}$ are –1.813 kcal/mol and –2.67 eV for the C-I bond homolytic dissociation and one-electron reduction reactions, respectively. Thus, the DFT calculated reduction potential of $E^{\theta}_{\mathrm{ArI/Ar}^{\bullet}+\mathrm{I}^{-}}$ is –1.43 V.

Note S1.3 Act-2 PC–ArI activation process

In this activation process, the ArI species, which is the product of Act-1 activation ($\mathrm{Ar_2I}^{\bullet} \to \mathrm{Ar}^{\bullet} + \mathrm{ArI}$), will act as the acceptor to further activate the PCs. The activation reactions are shown as follows.

$\mathrm{PC} \to \mathrm{PC}^{*}$;

$\mathrm{PC}^{*} + \mathrm{ArI} \to \mathrm{PC}^{\bullet +} + \mathrm{Ar}^{\bullet} + \mathrm{I}^{-}$

With the obtained reduction potential of $E^{\theta}_{\mathrm{ArI/Ar^{\bullet}+I^{-}}}$, the reaction free energy in this activation process can be obtained.

$$\Delta_{\mathrm{r}}G^{\theta} = F\left(E^{\theta}_{\mathrm{PC^{\bullet+}/PC*}} - E^{\theta}_{\mathrm{ArI/Ar^{\bullet}+I^{-}}}\right) - \frac{N_{\mathrm{A}}e^{2}}{4\pi\varepsilon_{0}\varepsilon r}$$

$$r = r_{\mathrm{PC*}} + r_{\mathrm{ArI}}$$

$\Delta_{\mathrm{r}}G^{\theta}$ of Ph-DTP and TPA-DTP are calcualted to be 7.26 kcal mol^{-1} and 4.16 kcal mol^{-1}, respectively. Its solvent reorganization energy can be obtained by eq S9 using the parameters shown in Table S1.

$$\lambda_{0} = 95\left(\frac{1}{2r_{\mathrm{PC*}}} + \frac{1}{2r_{\mathrm{eff}}} - \frac{1}{r_{\mathrm{PC*}}+r_{\mathrm{eff}}}\right)$$

The calculated λ_0 of Ph-DTP and TPA-DTP are 12.07 kcal/mol and 12.4 kcal/mol, respectively. In this activation process, with the calculated D_{B} and D_{p} of ArI as shown in Table S1, the intrinsic barrier $\Delta G_0^{\ddagger}$ and the activation free energy $\Delta G^{\ddagger}$ can be calculated by the following equations.

$$\Delta G_{0}^{\ddagger} = \frac{\lambda_{0} + \left(\sqrt{D_{\mathrm{B\text{-}ArI}}} - \sqrt{D_{\mathrm{p\text{-}ArI}}}\right)^{2}}{4}$$

The intrinsic barrier $\Delta G_0^{\ddagger}$ of Ph-DTP and TPA-DTP are calcualted to be 8.69 kcal/mol and 8.77 kcal/mol, respectively.

$$\Delta G^{\ddagger} = \Delta G_{0}^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta} - D_{\mathrm{p}}}{4\Delta G_{0}^{\ddagger}}\right)^{2}$$

The activation free energy $\Delta G^{\ddagger}$ of Ph-DTP and TPA-DTP are then obtained to be 11.9 kcal mol^{-1} and 10.24 kcal mol^{-1}, respectively.

In Act-2 activation, μ are 163.43 g mol^{-1} and 194.62 g mol^{-1} in Ph-DTP and TPA-DPT activation processes, respectively. The pre-exponential factor Z of each activation process can be obtained by

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\left(r_{\mathrm{Ph\text{-}DTP*}} + r_{\mathrm{ArI}}\right)^{2}$$

Z of Ph-DTP and TPA-DTP are 8.66×10^{11} M^{-1}s^{-1} and 1.33×10^{12} M^{-1}s^{-1}, respectively.

Based on the above parameters, the rate constant k_{act} and quantum yield φ_{act} can be obtained.

The concentration of ArI needs to be estimated, and is hereby considered to be around 10% of that of Ar_2I^+.

$$k_{\mathrm{act}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

The rate constant k_{act} of Ph-DTP and TPA-DTP are calculted to be 1.64×10^3 $M^{-1}s^{-1}$ and 4.14×10^4 $M^{-1}s^{-1}$, respectively.

$$\varphi_{\mathrm{act}} = k_{\mathrm{act}}[\mathrm{ArI}]\tau_0 \Phi_{\mathrm{F}}$$

The quantum yield φ_{act} of Ph-DTP and TPA-DTP are 1.33×10^{-8} and 2.72×10^{-7}, respectively.

Note S1.4 Act-3 PC–EDB activation process

Different to Act-1 and Act-2, in the Act-3 activation process, EDB is the donor while PCs* are the acceptors. The electrons transfer from the donor to the acceptor to form $PC^{\bullet-}$ and $EDB^{\bullet+}$ species. Lalevée *et al.* have conjectured that one $H^{\bullet}$ will break away from $EDB^{\bullet+}$, forming $EDB^{\bullet}(–H) + H^+$.[16] However, the calculated bond dissociation energy of $EDB^{\bullet+} \rightarrow EDB^{\bullet}(–H) + H^+$ is 177.08 kcal/mol, which demonstrates that it is hard to obtain the dissociative $EDB^{\bullet}(–H)$ and H^+. In this activation path, the reactions are shown as follows.

$PC \rightarrow PC^*$;

$PC^* + EDB \rightarrow PC^{\bullet-} + EDB^{\bullet+}$

Similar to the oxidation potential of DTPs, the oxidation potential of EDB can be calculated with the following equation, where the DFT calculated $E^{\theta}_{\mathrm{EDB}^{\bullet+}/\mathrm{EDB}}$ is 0.855 V. Then, $E^{\theta}_{\mathrm{EDB}^{\bullet+}/\mathrm{EDB}^*}$ can be calculated based on the results of $E^{\theta}_{\mathrm{EDB}^{\bullet+}/\mathrm{EDB}}$ and the maximum emission wavelength shown in Fig. 1.

$$E^{\theta}_{\mathrm{EDB}^{\bullet+}/\mathrm{EDB}^*} = E^{\theta}_{\mathrm{EDB}^{\bullet+}/\mathrm{EDB}} - E_{h\upsilon} = 0.855\ \mathrm{V} - (6.63 \times 10^{-34}\ \mathrm{J\ s} \times 3 \times 10^{8}\ \mathrm{m/s})/(323\ \mathrm{nm} \times 1.602 \times 10^{-19}\ \mathrm{C}) = -2.99\ \mathrm{V}$$

The DFT calculated $E^{\theta}_{\mathrm{PC}^*/\mathrm{PC}^{\bullet-}}$ are –1.72 V and –1.77 V for Ph-DTP and TPA-DTP as shown in Table 1, and the reaction free energy of each PC in the Act-3 process can be obtained by

$$\Delta_{\mathrm{r}}G^{\theta} = F\left(E^{\theta}_{\mathrm{EDB}^{\bullet+}/\mathrm{EDB}^{*}} - E^{\theta}_{\mathrm{PC}^{*}/\mathrm{PC}^{\bullet-}}\right) - \frac{N_{\mathrm{A}}e^{2}}{4\pi\varepsilon_{0}\varepsilon r}$$

$\Delta_{\mathrm{r}}G^{\theta}$ of Ph-DTP and TPA-DTP are –124.79 kcal mol^{-1} and –119.48 kcal mol^{-1}, respectively. The solvent reorganization energy can be obtained by eq S9 using the parameters shown in Table S1.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{PC}^*}} + \frac{1}{2r_{\mathrm{EDB}}} - \frac{1}{r_{\mathrm{PC}^*}+r_{\mathrm{EDB}}}\right)$$

λ_0 of Ph-DTP and TPA-DTP are 6.08 kcal/mol and 5.73 kcal/mol, respectively.

In the main activation process PC* + EDB → PC$^{\bullet-}$ + EDB$^{\bullet+}$, the intrinsic barrier $\Delta G_0^{\ddagger}$ and the activation free energy $\Delta G^{\ddagger}$ can be calculated by the following equations,

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

The intrinsic barrier $\Delta G_0^{\ddagger}$ of Ph-DTP and TPA-DTP are calculated to be 1.52 kcal/mol and 1.43 kcal/mol, respectively.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

The activation free energy $\Delta G^{\ddagger}$ of Ph-DTP and TPA-DTP are calculated to be 579.44 kcal mol^{-1} and 565.62 kcal mol^{-1}, respectively.

In Act-3 activation, μ are 134.15 g mol^{-1} and 154.48 g mol^{-1} in Ph-DTP and TPA-DPT activation processes, respectively. The pre-exponential factor Z of each activation process can be obtained by

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\,(r_{\text{Ph-DTP*}} + r_{\mathrm{EDB}})^2$$

Z of Ph-DTP and TPA-DTP are 1.11 × 10^{12} M^{-1}s^{-1} and 1.67 × 10^{12} M^{-1}s^{-1}, respectively.

Based on the above parameters, the rate constant k_{act} and quantum yield φ_{act} can be obtained. Particularly, in the quantum yield calculation, the concentration of DTPs is 100 times lower than that of Ar$_2$I$^+$ (0.01% PC/1% Ar$_2$I$^+$ in experimental conditions). According to

$$k_{\mathrm{act}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

the rate constant k_{act} of Ph-DTP and TPA-DTP are both nearly 0, and consequently, their quantum yields φ_{act} are also around zero.

Such high activation barrier and ultra-low quantum yield indicate that the activation process Act-3 is hard to carry out, which means that it is in fact difficult for both DTPs* to be activated by EDB.

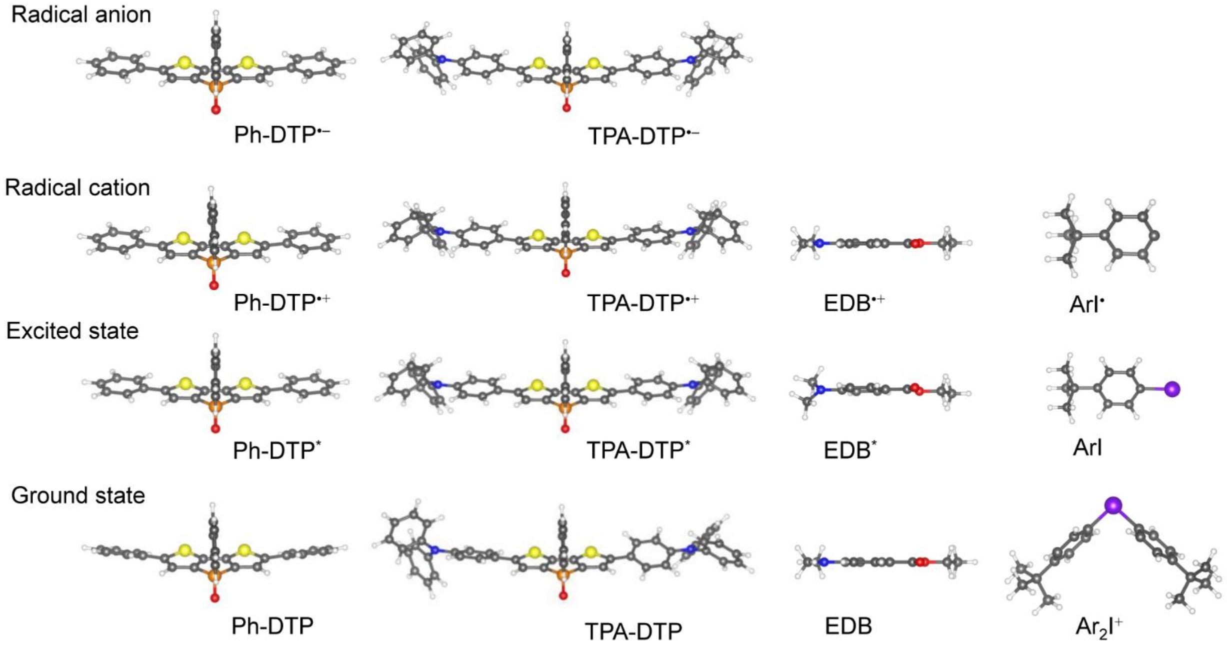

Fig. S1 Stable structures of the DTPs in the ground state and excited state, oxidized radical cations and radical anions shown in the activation processes, as well as the relevant structures of the electron donor EDB/acceptor Ar_2I^+ (gray: C, white: H, yellow: S, red: O, aurantia: P, blue N, purple: I).

Note S2. Calculations of activation energies for deactivation pathways

Note S2.1 Rate of biradical termination

The rate constant of biradical termination is estimated from $R_t = k_t[P_n^\bullet]^2 = 10^7\ \mathrm{M^{-1}s^{-1}} \times (4.62\times10^{-8}\ \mathrm{M})^2 = 2.1\times10^{-8}\ \mathrm{Ms^{-1}}$, where $[P_n^\bullet]$ is the concentration of the propagating radical and can be calculated from $k_p^{\mathrm{app}} = k_p[P_n^\bullet]$, using k_p and k_p^{app} values of $10^3\ \mathrm{M^{-1}s^{-1}}$ and $4.62\times10^{-5}\ \mathrm{s^{-1}}$, respectively, where k_p^{app} is the apparent rate constant of propagation.[11] Here, for calculation, $[P_n^\bullet]$ will be taken as the concentration of Ar$^{\bullet}$, since Ar$^{\bullet}$ acts as the initiating species for radical polymerization. As shown in Pan's work,[11] the conversion of PC (Ph-PTZ) is about 45% at 4 h, while in Mousawi's result[17], the conversion of PC (TPA-DTP) is about 80% at 200 s. Clearly, the DTP-based PCs have faster k_p^{app} than the Ph-PTZ-based PC. Since no experimental data on the k_p^{app} value of DTP-based PCs have been reported, here, for the basis of calculation and comparison, the values of k_p^{app} and [Ar$^{\bullet}$] are taken to be 4.62×10^{-5} s^{-1} and 4.62×10^{-8} M as the lowest limit thresholds. R_t is then used to compare this termination rate to each deactivation rate. In a controlled process, the rate of the deactivation process should be faster than that of biradical termination.

Note S2.2 Deactivation processes in the two-component PC-Ar$_2$I$^+$ system

Path A1 – OSET-I deactivation

$DTP^{\bullet+} + Ar^{\bullet} + ArI \rightarrow DTP + Ar_2I^+$

$\Delta G_0^{\ddagger}$ and λ_0 are the same as the values in the Act-1 path. $\Delta_r G^{\theta}$ is the calculated reaction free energy, and is –32.196 kcal/mol for the Ph-DTP reaction and –24.21 kcal/mol for the TPA-DTP reaction.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta} - D_p}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 1.586 kcal/mol × (1 – (32.196+0.86)/(4×1.586))^2 = 28.12 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 1.481 kcal/mol × (1 – (24.21+0.86)/(4×1.481))^2 = 15.47 kcal/mol

$$Z = N_A^2 8\pi^2 \sqrt{\frac{2RT}{\pi}}\left[\left(\frac{m_A+m_B}{m_A m_B}\right)^{\frac{1}{2}} + \left(\frac{m_B+m_C}{m_B m_C}\right)^{\frac{1}{2}}\right] d_{A\leftrightarrow B}^2 d_{B\leftrightarrow C}^2 \delta$$

where A, B and C are the three species involved in the reaction. d is the center to center distance between the subscript species. δ is the distance between the first two spheres when hit by the third one. δ is usually in the range of 0.3[1] to 1.0 Å.[18] The smaller value of 0.3 Å is used here. In this equation, A is defined as DTP$^{\bullet+}$, B as Ar$^{\bullet}$ and C as ArI.

Z (Ph-DTP) = $(6.022\times10^{23}$ mol$^{-1})^2\times8\times3.14^2\times(2\times8.314$ Jmol^{-1}K$^{-1}\times298.15$ K/3.14$)^{1/2}\times$\{[(0.44 kgmol^{-1} +0.133 kgmol^{-1})/(0.44 kgmol$^{-1}\times$0.133 kgmol^{-1})]$^{1/2}$ + [(0.133 kgmol^{-1}+0.26 kgmol^{-1})/(0.133 kgmol$^{-1}\times$0.26 kgmol^{-1})]$^{1/2}$\}×(14.118 Å)^2×(10.343 Å)^2×0.3 Å = 4.73×10^{11} M^{-2}s^{-1}

Z (TPA-DTP) = $(6.022\times10^{23}$ mol$^{-1})^2\times8\times3.14^2\times(2\times8.314$ Jmol^{-1}K$^{-1}\times298.15$ K/3.14$)^{1/2}\times$\{[(0.774

kgmol^{-1} +0.133 kgmol^{-1})/(0.774 kgmol^{-1}×0.133 kgmol^{-1})]$^{1/2}$ + [(0.133 kgmol^{-1}+0.26 kgmol^{-1})/(0.133 kgmol^{-1}×0.26 kgmol^{-1})]$^{1/2}$}×(18.554 Å)^2×(10.343 Å)^2×0.3 Å = 7.96×10^{11} $\text{M}^{-2}\text{s}^{-1}$

According to

$$k_{\text{A1}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A1} (Ph-DTP) = 4.73×10^{11} $\text{M}^{-2}\text{s}^{-1}$ × exp(–28.12 kcal mol^{-1}/(8.314 $\text{Jmol}^{-1}\text{K}^{-1}$ ×298.15 K)) = 1.15×10^{-9} $\text{M}^{-2}\text{s}^{-1}$

k_{A1} (TPA-DTP) = 7.96×10^{11} $\text{M}^{-2}\text{s}^{-1}$ × exp(–15.47 kcal mol^{-1}/(8.314 $\text{Jmol}^{-1}\text{K}^{-1}$ ×298.15 K)) = 3.63 $\text{M}^{-2}\text{s}^{-1}$

The concentration of $\text{DTP}^{\bullet+}$ cannot be directly detected in electrochemical measurements. Therefore, about 10% of termination is considered here, such that a low concentration of 1.84×10^{-5} M is used for [$\text{DTP}^{\bullet+}$], and 1.84×10^{-3} M for [ArI].

$R_{\text{A1}} = k_{\text{A1}}$ [$\text{DTP}^{\bullet+}$][$\text{Ar}^{\bullet}$][ArI]

R_{A1} (Ph-DTP) = 1.15×10^{-9} $\text{M}^{-2}\text{s}^{-1}$×$1.84\times10^{-5}$ M×4.62×10^{-8} M×1.84×10^{-3} M = 1.8×10^{-24} Ms^{-1}

R_{A1} (TPA-DTP) = 3.63 $\text{M}^{-2}\text{s}^{-1}$×$1.84\times10^{-5}$ M×4.62×10^{-8} M×1.84×10^{-3} M = 5.68×10^{-15} Ms^{-1}

R/R_{t} (Ph-DTP) = 1.8×10^{-24} /2.1×10^{-8} = 8.57×10^{-17}

R/R_{t} (TPA-DTP) =5.68×10^{-15}/2.1×10^{-8} = 2.7×10^{-7}

Path A2 – OSET-II deactivation

A2-a. $\text{DTP}^{\bullet+} + \text{Ar}^{\bullet} \rightarrow \text{DTP} + \text{Ar}^{+}$;

A2-b. $\text{Ar}^{+} + \text{ArI} \rightarrow \text{Ar}_2\text{I}^{+}$

The calculated radii of $\text{DTP}^{\bullet+}$ and $\text{Ar}^{\bullet}$ are 9.497 Å (Ph-$\text{DTP}^{\bullet+}$), 13.933 Å (TPA-$\text{DTP}^{\bullet+}$) and 4.621 Å ($\text{Ar}^{\bullet}$), respectively. The solvent reorganization energy can be calculated by

$$\lambda_0 = 95\left(\frac{1}{2r_{\text{DTP}^{\bullet+}}} + \frac{1}{2r_{\text{Ar}^{\bullet}}} - \frac{1}{r_{\text{DTP}^{\bullet+}}+r_{\text{Ar}^{\bullet}}}\right)$$

λ_0 of Ph-DTP is 8.58 kcal/mol, and 8.57 kcal/mol for TPA-DTP.

$\Delta_{\text{r}}G^{\theta}$ is the calculated reaction free energy of the A2-a reaction, where $\Delta_{\text{r}}G^{\theta}$ (Ph-DTP) is 5.468 kcal/mol and $\Delta_{\text{r}}G^{\theta}$ (TPA-DTP) is 13.457 kcal/mol.

According to $\Delta G_0^{\ddagger} = \lambda_0/4$

$\Delta G_0^{\ddagger}$ is 2.145 kcal/mol for Ph-DTP, and 2.14 kcal/mol for TPA-DTP. According to

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ P is 5.75 kcal/mol for Ph-DT, and 14.16 kcal/mol for TPA-DTP.

In the reaction $DTP^{\bullet+} + Ar^{\bullet} \underset{k_2}{\rightleftarrows} DTP + Ar^{+}$, the reaction equilibrium constant k_f can be calculated by $k_f = \frac{k_1}{k_2} = e^{-\frac{\Delta r G^{\theta}}{RT}}$,where

$$k_1 = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_1 of Ph-DTP and TPA-DTP are 5.685×10^7 $M^{-1}s^{-1}$ and 64.14 $M^{-1}s^{-1}$, respectively.

k_f(Ph-DTP) = $\exp(-\Delta_r G^{\theta}/RT) = 9.768\times10^{-5}$

k_f (TPA-DTP) = $\exp(-\Delta_r G^{\theta}/RT) = 1.36\times10^{-10}$

k_2 (Ph-DTP) = $k_1/k_f = 5.82\times10^{11}$ $M^{-1}s^{-1}$

k_2 (TPA-DTP) = $k_1/k_f = 4.72\times10^{11}$ $M^{-1}s^{-1}$

This confirms that the reaction between DTP and Ar^{+} is faster than that between $DTP^{\bullet+}$ and $Ar^{\bullet}$ ($k_2 > k_1$).

$$Z\,(\text{Ph-DTP}) = N_A\sqrt{\frac{8\pi RT}{\mu}}\,(r_{DTP} + r_{ArI})^2$$

Z is 9.37×10^{11} $M^{-1}s^{-1}$ for Ph-DTP, and 1.54×10^{12} $M^{-1}s^{-1}$ for TPA-DTP.

$$\mu = \frac{M_{DTP^{\bullet+}} M_{Ar^{\bullet}}}{M_{DTP^{\bullet+}} + M_{Ar^{\bullet}}}$$

μ of Ph-DTP is 102.13 g mol^{-1}, and 113.5 g mol^{-1} for TPA-DTP.

Then R_1, calculated by $k_1[DTP^{\bullet+}][Ar^{\bullet}]$, is 4.83×10^{-5} Ms^{-1} for Ph-DTP, and 5.45×10^{-11} Ms^{-1} for TPA-DTP.

In the A2-b reaction, $Ar^{+} + ArI \xrightarrow{k_{diff}} Ar_2I^{+}$

$$k_{diff} = \frac{8RT}{3\eta}$$

$k_{diff} = 1.787\times10^{10}$ $M^{-1}s^{-1}$

$$\frac{d[Ar^{+}]}{dt} = k_1[DTP^{\bullet+}][Ar^{\bullet}] - k_2[DTP][Ar^{+}] - k_{diff}[Ar^{+}][ArI] = 0$$

$$[\mathrm{Ar}^{+}] = \frac{k_1[\mathrm{DTP}^{\bullet+}][\mathrm{Ar}^{\bullet}]}{k_2[\mathrm{DTP}]+k_{\mathrm{diff}}[\mathrm{ArI}]}$$

$[\mathrm{Ar}^{+}]$ (Ph-DTP) = 5.685×10^{7} $\mathrm{M^{-1}s^{-1}}\times1.84\times10^{-5}$ M$\times4.62\times10^{-8}$ M/(5.82×10^{11} $\mathrm{M^{-1}s^{-1}}\times1.84\times10^{-4}$ M + 1.787×10^{10} $\mathrm{M^{-1}s^{-1}}\times1.84\times10^{-3}$ M) = 3.453×10^{-13} M

$[\mathrm{Ar}^{+}]$ (TPA-DTP) = 64.14 $\mathrm{M^{-1}s^{-1}}\times1.84\times10^{-5}$ M$\times4.62\times10^{-8}$ M/(4.72×10^{11} $\mathrm{M^{-1}s^{-1}}\times1.84\times10^{-4}$ M + 1.787×10^{10} $\mathrm{M^{-1}s^{-1}}\times1.84\times10^{-3}$ M) = 4.55×10^{-19} M

$R_{\mathrm{overall}} = k_{\mathrm{diff}}[\mathrm{Ar}^{+}][\mathrm{ArI}]$

R_{overall} (Ph-DTP) = 1.787×10^{10} $\mathrm{M^{-1}s^{-1}}\times3.453\times10^{-13}$ M$\times1.84\times10^{-3}$ M = 1.14×10^{-5} $\mathrm{Ms^{-1}}$

R_{overall} (TPA-DTP) = 1.787×10^{10} $\mathrm{M^{-1}s^{-1}}\times4.55\times10^{-19}$ M$\times1.84\times10^{-3}$ M = 1.5×10^{-11} $\mathrm{Ms^{-1}}$

R/R_{t} (Ph-DTP) = 1.14×10^{-5} $\mathrm{Ms^{-1}}/2.1\times10^{-8}$ $\mathrm{Ms^{-1}}$ = 543

R/R_{t} (TPA-DTP) = 1.5×10^{-11} $\mathrm{Ms^{-1}}/2.1\times10^{-8}$ $\mathrm{Ms^{-1}}$ = 7.14×10^{-4}

Path A3 – ISET deactivation

$\mathrm{DTP}^{\bullet+}\text{-ArI} + \mathrm{Ar}^{\bullet} \rightarrow \mathrm{DTP} + \mathrm{Ar_2I^{+}}$

The calculated radii of $\mathrm{DTP}^{\bullet+}$-ArI and $\mathrm{Ar}^{\bullet}$ are 9.491 Å (Ph-$\mathrm{DTP}^{\bullet+}$-ArI), 13.905 Å (TPA-$\mathrm{DTP}^{\bullet+}$ -ArI) and 4.621 Å ($\mathrm{Ar}^{\bullet}$), respectively. The solvent reorganization energy can be calculated by

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{DTP}^{\bullet+}\text{-ArI}}} + \frac{1}{2r_{\mathrm{Ar}^{\bullet}}} - \frac{1}{r_{\mathrm{DTP}^{\bullet+}\text{-ArI}}+r_{\mathrm{Ar}^{\bullet}}}\right)$$

λ_0 (Ph-DTP) = 8.55 kcal/mol, and λ_0 (TPA-DTP) = 8.57 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\mathrm{B}}}{4}$$

D_{B} is the bond dissociation energy of $\mathrm{DTP}^{\bullet+}$-ArI with the value of 7.5 kcal/mol for Ph-DTP and 6.98 kcal/mol for TPA-DTP.

Then $\Delta G_0^{\ddagger}$ (Ph-DTP) is calculated to be 4.013 kcal/mol, and $\Delta G_0^{\ddagger}$ (TPA-DTP) is 3.89 kcal/mol. $\Delta_{\mathrm{r}}G^{\theta}$ is the calculated reaction free energy, where $\Delta_{\mathrm{r}}G^{\theta}$(Ph-DTP) = –45.66 kcal/mol and $\Delta_{\mathrm{r}}G^{\theta}$(TPA-DTP) = –29.08 kcal/mol.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 13.65 kcal/mol, and $\Delta G^{\ddagger}$ (TPA-DTP) = 2.94 kcal/mol

$$\mu = \frac{M_{\mathrm{DTP}^{\bullet+}\text{-ArI}}M_{\mathrm{Ar}^{\bullet}}}{M_{\mathrm{DTP}^{\bullet+}\text{-ArI}}+M_{\mathrm{Ar}^{\bullet}}}$$

μ (Ph-DTP) = 111.76 g mol^{-1}, and μ (TPA-DTP) = 117.84 g mol^{-1}

$$Z = N_A \sqrt{\frac{8\pi RT}{\mu}} (r_{DTP^{\bullet +}\text{-ArI}} + r_{Ar^{\bullet}})^2$$

Z (Ph-DTP) = 8.95 $\times 10^{11}$ $M^{-1}s^{-1}$, Z (TPA-DTP) = 1.5×10^{12} $M^{-1}s^{-1}$

Calculation for the concentration of $DTP^{\bullet +}$-ArI:

$DTP^{\bullet +}$ + ArI ↔ $DTP^{\cdot +}$-ArI   (RA3-M)

Reaction equilibrium constant k_f of RA3-M:

$$k_f = e^{-\frac{\Delta_r G^{\theta}(\text{RA3-M})}{RT}} = \frac{[DTP^{\bullet +}\text{-ArI}]}{[DTP^{\bullet +}][\text{ArI}]}$$

$\Delta_r G^{\theta}$ is the DFT calculated reaction free energy of RA3-M, where $\Delta_r G^{\theta}$(Ph-DTP) = 13.46 kcal/mol, and $\Delta_r G^{\theta}$(TPA-DTP) = 4.88 kcal/mol.

k_f (Ph-DTP) = exp(– $\Delta_r G^{\theta}_{\text{(RA3-M)}}$/RT) = 1.36×10^{-10}, k_f (TPA-DTP) = 2.65×10^{-4}

[Ph-$DTP^{\bullet +}$-ArI] = k_f [Ph-$DTP^{\bullet +}$][ArI] = 4.6×10^{-18} M

[TPA-$DTP^{\bullet +}$-ArI] = k_f [TPA-$DTP^{\bullet +}$][ArI] = 8.97×10^{-12} M

$$k_{A3} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A3} (Ph-DTP) = 88.16 $M^{-1}s^{-1}$, k_{A3} (TPA-DTP) = 1.05×10^{10} $M^{-1}s^{-1}$

$R_{A3} = k_{A3}$ [$DTP^{\cdot +}$-ArI][$Ar^{\bullet}$]

R_{A3} (Ph-DTP) = 1.87×10^{-23} Ms^{-1}, R_{A3} (TPA-DTP) = 4.35×10^{-9} Ms^{-1}

R/R_t (Ph-DTP) = 8.9×10^{-16}, R/R_t (TPA-DTP) = 0.21

Path A4 – DET deactivation

A4-a: $DTP^{\bullet +}$-ArI + $Ar^{\bullet}$ → DTP + ArI + Ar^{+};

A4-b: Ar^{+} + ArI → Ar_2I^{+}

λ_0, D_B, $\Delta G_0^{\ddagger}$, Z and μ are the same as the values shown in path A3. $\Delta_r G^{\theta}$ is the calculated reaction free energy, where $\Delta_r G^{\theta}$(Ph-DTP) is –8.0 kcal/mol and $\Delta_r G^{\theta}$(TPA-DTP) is 8.58 kcal/mol.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 1.01 kcal/mol, and $\Delta G^{\ddagger}$ (TPA-DTP) = 9.36 kcal/mol

$$k_{\mathrm{A4}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A4} (Ph-DTP) = 1.63×10^{11} $\mathrm{M^{-1}s^{-1}}$ and k_{A4} (TPA-DTP) = 2.06×10^{5} $\mathrm{M^{-1}s^{-1}}$

$R_{\mathrm{A4}} = k_{\mathrm{A4}}$ [DTP$^{\cdot+}$-ArI][Ar$^{\bullet}$]

R_{A4} (Ph-DTP) = 3.46×10^{-14} $\mathrm{Ms^{-1}}$ and R_{A4} (TPA-DTP) = 8.5×10^{-14} $\mathrm{Ms^{-1}}$

R/R_{t} (Ph-DTP) = 1.65×10^{-6}, and R/R_{t} (TPA-DTP) = 4.05×10^{-6}

Path A5 – OSET-III deactivation

A5-a. DTP$^{\bullet+}$-ArI + Ar$^{\bullet}$ → DTP-ArI + Ar^{+}

A5-b. DTP-ArI → DTP + ArI

A5-c. Ar^{+} + ArI → $\mathrm{Ar_2I^+}$

In step A5-a, $\Delta_{\mathrm{r}}G^{\theta}$ is the calculated reaction free energy, where $\Delta_{\mathrm{r}}G^{\theta}$(Ph-DTP) is –3.86 kcal/mol and $\Delta_{\mathrm{r}}G^{\theta}$(TPA-DTP) is 12.2 kcal/mol. λ_0, Z and μ are the same as the values shown in paths A3 and A4.

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 2.14 kcal/mol and $\Delta G_0^{\ddagger}$ (TPA-DTP) = 2.14 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 0.64 kcal/mol and $\Delta G^{\ddagger}$ (TPA-DTP) = 12.58 kcal/mol

$$k_{\mathrm{A5}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A5} (Ph-DTP) = 3.04×10^{11} $\mathrm{M^{-1}s^{-1}}$ and k_{A5} (TPA-DTP) = 8.99×10^{2} $\mathrm{M^{-1}s^{-1}}$

$R_{\mathrm{A5}} = k_{\mathrm{A5}}$ [DTP$^{\cdot+}$-ArI][Ar$^{\bullet}$]

R_{A5} (Ph-DTP) = 6.46×10^{-14} $\mathrm{Ms^{-1}}$, and R_{A5} (TPA-DTP) = 3.73×10^{-16} $\mathrm{Ms^{-1}}$

R/R_{t} (Ph-DTP) = 3.08×10^{-6} and R/R_{t} (TPA-DTP) = 1.77×10^{-8}

Path A6 – AET deactivation

DTP$^{\bullet+}$ + Ar$^{\bullet}$ + I^{-} → DTP + ArI

$\Delta G_0^{\ddagger}$ is the same as the one shown in path Act-2, with the value of 8.69 kcal/mol for Ph-DTP and 8.77 kcal/mol for TPA-DTP. $\Delta_r G^{\theta}$ is the calculated reaction free energy, where $\Delta_r G^{\theta}$(Ph-DTP) = –57.49 kcal/mol and $\Delta_r G^{\theta}$(TPA-DTP) = –49.5 kcal/mol.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta} - D_p}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 4.17 kcal/mol, $\Delta G^{\ddagger}$ (TPA-DTP) = 1.77 kcal/mol.

$$Z = N_A^2 8\pi^2 \sqrt{\frac{2RT}{\pi}}\left[\left(\frac{m_A+m_B}{m_A m_B}\right)^{\frac{1}{2}} + \left(\frac{m_B+m_C}{m_B m_C}\right)^{\frac{1}{2}}\right] d_{A\leftrightarrow B}^2 d_{B\leftrightarrow C}^2 \delta$$

Here, we define A = $DTP^{\bullet+}$, B = $Ar^{\bullet}$, and C = I^- for the calculation of Z.

Z (Ph-DTP) = $(6.022\times10^{23}\ mol^{-1})^2\times8\times3.14^2\times(2\times8.314\ Jmol^{-1}K^{-1}\times298.15\ K/3.14)^{1/2}\times\{[(0.44\ kgmol^{-1} +0.133\ kgmol^{-1})/(0.44\ kgmol^{-1}\times0.133\ kgmol^{-1})]^{1/2} + [(0.133\ kgmol^{-1}+0.127\ kgmol^{-1})/(0.133\ kgmol^{-1}\times0.127\ kgmol^{-1})]^{1/2}\}\times(14.118\ Å)^2\times(6.601\ Å)^2\times0.3\ Å = 2.09\times10^{11}\ M^{-2}s^{-1}$

Z (TPA-DTP) = $(6.022\times10^{23}\ mol^{-1})^2\times8\times3.14^2\times(2\times8.314\ Jmol^{-1}K^{-1}\times298.15\ K/3.14)^{1/2}\times\{[(0.774\ kgmol^{-1} +0.133\ kgmol^{-1})/(0.774\ kgmol^{-1}\times0.133\ kgmol^{-1})]^{1/2} + [(0.133\ kgmol^{-1}+0.127\ kgmol^{-1})/(0.133\ kgmol^{-1}\times0.127\ kgmol^{-1})]^{1/2}\}\times(18.554\ Å)^2\times(6.601\ Å)^2\times0.3\ Å = 3.52\times10^{11}\ M^{-2}s^{-1}$

$$k_{A6} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A6} (Ph-DTP) = $1.83\times10^{8}\ M^{-2}s^{-1}$, k_{A6} (TPA-DTP) = $1.77\times10^{10}\ M^{-2}s^{-1}$

$R_{A6} = k_{A6}\,[DTP^{\bullet+}][Ar^{\bullet}][I^-]$

R_{A6} (Ph-DTP) = $2.86\times10^{-8}\ Ms^{-1}$, and R_{A6} (TPA-DTP) = $2.77\times10^{-6}\ Ms^{-1}$

R/R_t (Ph-DTP) = 1.36 and R/R_t (TPA-DTP) = 132

Path A7 – OSET-II deactivation

A7-a: $DTP^{\cdot+} + Ar^{\cdot} \rightarrow DTP + Ar^+$

A7-b. $Ar^+ + I^- \rightarrow ArI$

The reaction of path A7-a is the same as that of A2-a, such that it has the same values of λ_0, $\Delta G_0^{\ddagger}$, $\Delta_r G^{\theta}$, $\Delta G^{\ddagger}$, Z, μ, k, and k_f. However, in path A7-b, $R_{overall}$ is the final generation rate of ArI and it equals to $k_{diff}[Ar^+][I^-]$. Here, the lower concentration of I^- (than [ArI] of path A2-b) leads to small values of R_{overall} and R/R_{t} for this path.

R_{overall} (Ph-DTP) = 1.787×10^{10} $\mathrm{M^{-1}s^{-1}}\times3.453\times10^{-13}$ $\mathrm{M}\times1.84\times10^{-4}$ M = 1.14×10^{-6} $\mathrm{Ms^{-1}}$

R_{overall} (TPA-DTP) = 1.787×10^{10} $\mathrm{M^{-1}s^{-1}}\times4.55\times10^{-19}$ $\mathrm{M}\times1.84\times10^{-4}$ M = 1.5×10^{-12} $\mathrm{Ms^{-1}}$

R/R_{t} (Ph-DTP) = 1.14×10^{-6} $\mathrm{Ms^{-1}}/2.1\times10^{-8}$ $\mathrm{Ms^{-1}}$ = 54

R/R_{t} (TPA-DTP) = 1.5×10^{-12} $\mathrm{Ms^{-1}}/2.1\times10^{-8}$ $\mathrm{Ms^{-1}}$ = 7.14×10^{-5}

Path A8 – ISET deactivation

$\mathrm{DTP^{\bullet+}\text{-}I^{-} + Ar^{\bullet} \rightarrow DTP + ArI}$

D_{B} is the bond dissociation energy of $\mathrm{DTP^{\bullet+}\text{-}I^{-}}$, with values of 15.61 kcal/mol and 7.18 kcal/mol for $\mathrm{Ph\text{-}DTP^{\bullet+}\text{-}I^{-}}$ and $\mathrm{TPA\text{-}DTP^{\bullet+}\text{-}I^{-}}$, respectively. $\Delta_{\mathrm{r}}G^{\theta}$ is the calculated reaction free energy; for the Ph-DTP case, it is –53.97 kcal/mol, and for the TPA-DTP case, it is –54.34 kcal/mol. The radii of $\mathrm{DTP^{\bullet+}\text{-}I^{-}}$ and $\mathrm{Ar^{\bullet}}$ are 9.54 Å ($\mathrm{Ph\text{-}DTP^{\bullet+}\text{-}I^{-}}$), 14.018 Å ($\mathrm{TPA\text{-}DTP^{\bullet+}\text{-}I^{-}}$) and 4.621 Å ($\mathrm{Ar^{\bullet}}$).

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}}} + \frac{1}{2r_{\mathrm{Ar^{\bullet}}}} - \frac{1}{r_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}}+r_{\mathrm{Ar^{\bullet}}}}\right)$$

λ_0 (Ph-DTP) = 8.55 kcal/mol and λ_0 (TPA-DTP) = 8.57 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\mathrm{B}}}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 6.04 kcal/mol, and $\Delta G_0^{\ddagger}$ (TPA-DTP) = 3.94 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 9.2 kcal/mol and $\Delta G^{\ddagger}$ (TPA-DTP) = 23.61 kcal/mol

$$\mu = \frac{M_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}}M_{\mathrm{Ar^{\bullet}}}}{M_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}}+M_{\mathrm{Ar^{\bullet}}}}$$

μ (Ph-DTP) = 107.73 g $\mathrm{mol^{-1}}$, μ (TPA-DTP) = 115.89 g $\mathrm{mol^{-1}}$

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\left(r_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}} + r_{\mathrm{Ar^{\bullet}}}\right)^2$$

Z (Ph-DTP) = 9.18×10^{11} $\mathrm{M^{-1}s^{-1}}$ and Z (TPA-DTP) = 1.534×10^{12} $\mathrm{M^{-1}s^{-1}}$

$$k_{\mathrm{A8}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A8} (Ph-DTP) = 1.65×10^{5} $\mathrm{M^{-2}s^{-1}}$, k_{A8} (TPA-DTP) = 7.55×10^{-6} $\mathrm{M^{-2}s^{-1}}$

The calculation of the concentration of $\mathrm{DTP^{\bullet+}\text{-}I^{-}}$:

$\text{DTP}^{\bullet+} + \text{I}^- \leftrightarrow \text{DTP}^{\bullet+}\text{-I}^-$ (RA8-M)

The reaction equilibrium constant k_f of RA8-M can be calculated by

$$k_f = e^{-\frac{\Delta_r G^{\theta}(\text{RA8-M})}{RT}} = \frac{[\text{DTP}^{\bullet+}\text{-I}^-]}{[\text{DTP}^{\bullet+}][\text{I}^-]}$$

where $\Delta_r G^{\theta}{}_{(\text{RA8-M})}$ is the DFT calculated free energy of reaction RA8-M; for the Ph-DTP case, it is –3.52 kcal/mol, while for the TPA-DTP case, it is 4.84 kcal/mol.

$k_f\,(\text{Ph-DTP}) = \exp(3.52\ \text{kcal mol}^{-1}/(1.987\ \text{calmol}^{-1}\text{K}^{-1}\times 298.15\ \text{K})) = 380.58$

$k_f\,(\text{TPA-DTP}) = \exp(-4.84\ \text{kcal mol}^{-1}/(1.987\ \text{calmol}^{-1}\text{K}^{-1}\times 298.15\ \text{K})) = 2.83\times 10^{-4}$

The concentration of $\text{DTP}^{\bullet+}\text{-I}^-$ can be obtained by

$[\text{Ph-DTP}^{\bullet+}\text{-I}^-] = k_f[\text{DTP}^{\bullet+}][\text{I}^-] = 1.3\times 10^{-6}$ M

$[\text{TPA-DTP}^{\bullet+}\text{-I}^-] = 9.58\times 10^{-13}$ M

$R_{\text{A8}} = k_{\text{A8}}\,[\text{DTP}^{\bullet+}\text{-I}^-][\text{Ar}^{\bullet}]$

R_{A8} (Ph-DTP) = 9.9×10^{-9} Ms^{-1}, R_{A8} (Ph-DTP) = 3.34×10^{-25} Ms^{-1}

R/R_{t} (Ph-DTP) = 0.47, R/R_{t} (TPA-DTP) = 1.59×10^{-17}

Path A9 – DET deactivation

A9-a. $\text{DTP}^{\bullet+}\text{-I}^- + \text{Ar}^{\bullet} \rightarrow \text{DTP} + \text{I}^- + \text{Ar}^+$;

A9-b. $\text{Ar}^+ + \text{I}^- \rightarrow \text{ArI}$

In path A9-a, $\Delta_r G^{\theta}$ is the DFT calculated free energy, it is 8.98 kcal/mol for the Ph-DTP case and 8.62 kcal/mol for the TPA-DTP case. λ_0, D_{B}, $\Delta G_0{}^{\ddagger}$, Z and μ are the same as the values in path A8.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 11.36 kcal/mol and $\Delta G^{\ddagger}$ (TPA-DTP) = 9.43 kcal/mol

$$k_{\text{A9}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A9} (Ph-DTP) = 4.32×10^{3} M^{-1}s^{-1}, k_{A9} (TPA-DTP) = 1.87×10^{5} M^{-1}s^{-1}

$R_{\text{A9}} = k_{\text{A9}}\,[\text{DTP}^{\bullet+}\text{-I}^-][\text{Ar}^{\bullet}]$

R_{A9} (Ph-DTP) = 2.59×10^{-10} Ms^{-1}, R_{A9} (TPA-DTP) = 8.28×10^{-15} Ms^{-1}

R/R_{t} (Ph-DTP) = 1.23×10^{-2}, R/R_{t} (TPA-DTP) = 3.94×10^{-7}

Path A10 – OSET-III deactivation

A10-a. $DTP^{\bullet +}\text{-}I^{-} + Ar^{\bullet} \rightarrow DTP\text{-}I^{-} + Ar^{+}$

A10-b. $DTP\text{-}I^{-} \rightarrow DTP+I^{-}$

A10-c. $Ar^{+} + I^{-} \rightarrow ArI$

In path A10-a, $\Delta_r G^{\theta}$ is the DFT calculated free energy; it is 12.69 kcal/mol for the Ph-DTP case and 13.36 kcal/mol for the TPA-DTP case. λ_0, Z and μ are the same as the values shown in paths A8 and A9.

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 2.14 kcal/mol and $\Delta G_0^{\ddagger}$ (TPA-DTP) = 2.143 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 13.19 kcal/mol and $\Delta G^{\ddagger}$ (TPA-DTP) = 14.03 kcal/mol

$$k_{A10} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{A10} (Ph-DTP) = 196 $M^{-1}s^{-1}$, k_{A10} (TPA-DTP) = 79.6 $M^{-1}s^{-1}$

$$R_{A10} = k_{A10}\,[DTP^{\bullet +}\text{-}I^{-}][Ar^{\bullet}]$$

R_{A10} (Ph-DTP) = 1.18×10^{-11} Ms^{-1}, R_{A10} (TPA-DTP) = 3.52×10^{-18} Ms^{-1}

R/R_t (Ph-DTP) = 5.62×10^{-4}, R/R_t (TPA-DTP) = 1.68×10^{-10}

Table S2. Calculated activation barriers of each proposed deactivation path, A1-A10

Path		$\Delta G^{\ddagger}$ (kcal/mol)	Path		$\Delta G^{\ddagger}$ (kcal/mol)
A1	Ph-DTP	28.12	A6	Ph-DTP	4.17
	TPA-DTP	15.47		TPA-DTP	1.77
A2	Ph-DTP	5.75	A7	Ph-DTP	5.75
	TPA-DTP	14.16		TPA-DTP	14.16
A3	Ph-DTP	13.65	A8	Ph-DTP	9.2
	TPA-DTP	2.94		TPA-DTP	23.61
A4	Ph-DTP	1.01	A9	Ph-DTP	11.36
	TPA-DTP	9.36		TPA-DTP	9.43
A5	Ph-DTP	0.64	A10	Ph-DTP	13.19
	TPA-DTP	12.58		TPA-DTP	14.03

Note S2.3 Deactivation processes in the three-component PC–Ar_2I^+–EDB system

Path B

$DTP^{\bullet+} + EDB \rightarrow DTP + EDB^{\bullet+}$

$\Delta_r G^{\theta}$ is the DFT calculated free energy; it is –6.44 kcal/mol for the Ph-DTP case and 1.55 kcal/mol for the TPA-DTP case. The calculated radii of $DTP^{\bullet+}$ and EDB are 9.497 Å (Ph-$DTP^{\bullet+}$), 13.933 Å (TPA-$DTP^{\bullet+}$) and 6.907 Å (EDB).

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{DTP}^{\bullet+}}} + \frac{1}{2r_{\mathrm{EDB}}} - \frac{1}{r_{\mathrm{DTP}^{\bullet+}} + r_{\mathrm{EDB}}}\right)$$

λ_0 (Ph-DTP) = 6.09 kcal/mol

λ_0 (TPA-DTP) = 5.73 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 1.52 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 1.43 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 0.005 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 2.31 kcal/mol

$$\mu = \frac{M_{\mathrm{DTP}^{\cdot+}}M_{\mathrm{EDB}}}{M_{\mathrm{DTP}^{\cdot+}}+M_{\mathrm{EDB}}}$$

μ (Ph-DTP) = 134.15 g mol^{-1}

μ (TPA-DTP) = 154.48 g mol^{-1}

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\,(r_{\mathrm{DTP}^{\cdot+}} + r_{\mathrm{EDB}})^2$$

Z (Ph-DTP) = 1.1×10^{12} $\mathrm{M}^{-1}\mathrm{s}^{-1}$

Z (TPA-DTP) = 1.66×10^{12} $\mathrm{M}^{-1}\mathrm{s}^{-1}$

$$k_{\mathrm{B}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

k_{B} (Ph-DTP) = 1.09×10^{12} $\mathrm{M}^{-1}\mathrm{s}^{-1}$

k_{B} (TPA-DTP) = 3.36×10^{10} $\mathrm{M}^{-1}\mathrm{s}^{-1}$

$R_{\mathrm{B}} = k_{\mathrm{B}}\,[\mathrm{DTP}^{\cdot+}][\mathrm{EDB}]$

The concentration of EDB is taken from experiment as 0.0513 M.

R_{B} (Ph-DTP) is calculated to be 1.03×10^{6} Ms^{-1}

R_{B} (TPA-DTP) is calculated to be 3.17×10^{4} Ms^{-1}

R/R_{t} (Ph-DTP) is calculated to be 4.9×10^{13}

R/R_{t} (TPA-DTP) is calculated to be 1.51×10^{12}

Path B'-1

$\mathrm{DTP}^{\bullet+}$-ArI + EDB → DTP + ArI + $\mathrm{EDB}^{\bullet+}$

In this step, $\Delta_r G^{\theta}$ is the calculated reaction free energy, where $\Delta_r G^{\theta}$(Ph-DTP case) is –19.9 kcal/mol and $\Delta_r G^{\theta}$(TPA-DTP case) is –3.32 kcal/mol. D_{B} is the bond dissociation energy of $\mathrm{DTP}^{\bullet+}$-ArI with the value of 7.5 kcal/mol for Ph-$\mathrm{DTP}^{\bullet+}$-ArI and 6.98 kcal/mol for TPA-$\mathrm{DTP}^{\bullet+}$-ArI. The calculated radii of $\mathrm{DTP}^{\bullet+}$-ArI are 9.491 Å for Ph-$\mathrm{DTP}^{\bullet+}$-ArI and 13.905 Å for TPA-$\mathrm{DTP}^{\bullet+}$-ArI.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{DTP}^{\bullet+}\text{-ArI}}} + \frac{1}{2r_{\mathrm{EDB}}} - \frac{1}{r_{\mathrm{DTP}^{\bullet+}\text{-ArI}}+r_{\mathrm{EDB}}}\right)$$

λ_0 (Ph-DTP) = 6.09 kcal/mol

λ_0 (TPA-DTP) = 5.73 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\mathrm{B}}}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 3.4 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 3.18 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}} G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 0.73 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 1.73 kcal/mol

$$\mu = \frac{M_{\mathrm{DTP}^{\bullet+}\text{-ArI}} M_{\mathrm{EDB}}}{M_{\mathrm{DTP}^{\bullet+}\text{-ArI}}+M_{\mathrm{EDB}}}$$

μ (Ph-DTP) = 151.29 g mol^{-1}

μ (TPA-DTP) = 162.64 g mol^{-1}

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\,(r_{\mathrm{DTP}^{\bullet+}\text{-ArI}} + r_{\mathrm{EDB}})^2$$

Z (Ph-DTP) = 1.04 $\times 10^{12}$ M^{-1}s^{-1}

Z (TPA-DTP) = 1.61$\times 10^{12}$ M^{-1}s^{-1}

$$k_{\mathrm{B'-1}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$k_{\mathrm{B'-1}}$ (Ph-DTP) = 3.03 $\times 10^{11}$ M^{-1}s^{-1}

$k_{\mathrm{B'-1}}$ (TPA-DTP) = 8.68 $\times 10^{10}$ M^{-1}s^{-1}

$R_{\mathrm{B'-1}} = k_{\mathrm{B'-1}}$ [DTP$^{\cdot+}$-ArI][EDB]

$R_{\mathrm{B'-1}}$ (Ph-DTP) = 7.15 $\times 10^{-8}$ Ms^{-1}

$R_{\mathrm{B'-1}}$ (TPA-DTP) = 3.99 $\times 10^{-2}$ Ms^{-1}

R/R_{t} (Ph-DTP) is calculated to be 3.4

R/R_{t} (TPA-DTP) is calculated to be 1.9$\times 10^{6}$

Path B’-2

$$\mathrm{DTP^{\bullet+}\text{-}I^{-} + EDB \rightarrow DTP + I^{-} + EDB^{\bullet+}}$$

In this path, $\Delta_r G^{\theta}$ is the DFT calculated free energy; it is –2.92 kcal/mol for the Ph-DTP case and –3.29 kcal/mol for the TPA-DTP case. D_B is the bond dissociation energy of $\mathrm{DTP^{\bullet+}\text{-}I^{-}}$, where Ph-$\mathrm{DTP^{\bullet+}\text{-}I^{-}}$ is 15.61 kcal/mol and TPA-$\mathrm{DTP^{\bullet+}\text{-}I^{-}}$ is 7.18 kcal/mol. The calculated radii of $\mathrm{DTP^{\bullet+}\text{-}I^{-}}$ are 9.54 Å for Ph-$\mathrm{DTP^{\bullet+}\text{-}I^{-}}$ and 14.018 Å for TPA-$\mathrm{DTP^{\bullet+}\text{-}I^{-}}$.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}}} + \frac{1}{2r_{\mathrm{EDB}}} - \frac{1}{r_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}}+r_{\mathrm{EDB}}}\right)$$

λ_0 (Ph-DTP) = 6.08 kcal/mol

λ_0 (TPA-DTP) = 5.73 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_B}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 5.42 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 3.23 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 4.06 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 1.79 kcal/mol

$$\mu = \frac{M_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}} M_{\mathrm{EDB}}}{M_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}} + M_{\mathrm{EDB}}}$$

μ (Ph-DTP) = 143.99 g $\mathrm{mol^{-1}}$

μ (TPA-DTP) = 158.95 g $\mathrm{mol^{-1}}$

$$Z = N_A \sqrt{\frac{8\pi RT}{\mu}}\,(r_{\mathrm{DTP^{\bullet+}\text{-}I^{-}}} + r_{\mathrm{Ar^{\bullet}}})^2$$

Z (Ph-DTP) = 1.07×10^{12} $\mathrm{M^{-1}s^{-1}}$

Z (TPA-DTP) = 1.65×10^{12} $\mathrm{M^{-1}s^{-1}}$

$$k_{\mathrm{B'\text{-}2}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$k_{\mathrm{B'\text{-}2}}$ (Ph-DTP) = 1.13×10^{9} $\mathrm{M^{-1}s^{-1}}$

$k_{\mathrm{B'\text{-}2}}$ (TPA-DTP) = 8.04×10^{10} $\mathrm{M^{-1}s^{-1}}$

$$R_{\mathrm{B'\text{-}2}} = k_{\mathrm{B'\text{-}2}}\,[\mathrm{DTP^{\bullet+}\text{-}I^{-}}][\mathrm{EDB}]$$

$R_{\mathrm{B'\text{-}2}}$ (Ph-DTP) = 75.36 $\mathrm{Ms^{-1}}$

$R_{\mathrm{B'\text{-}2}}$ (TPA-DTP) = 3.95×10^{-3} Ms^{-1}

R/R_{t} (Ph-DTP) is calculated to be 3.59×10^{9}

R/R_{t} (TPA-DTP) is calculated to be 1.88×10^{5}

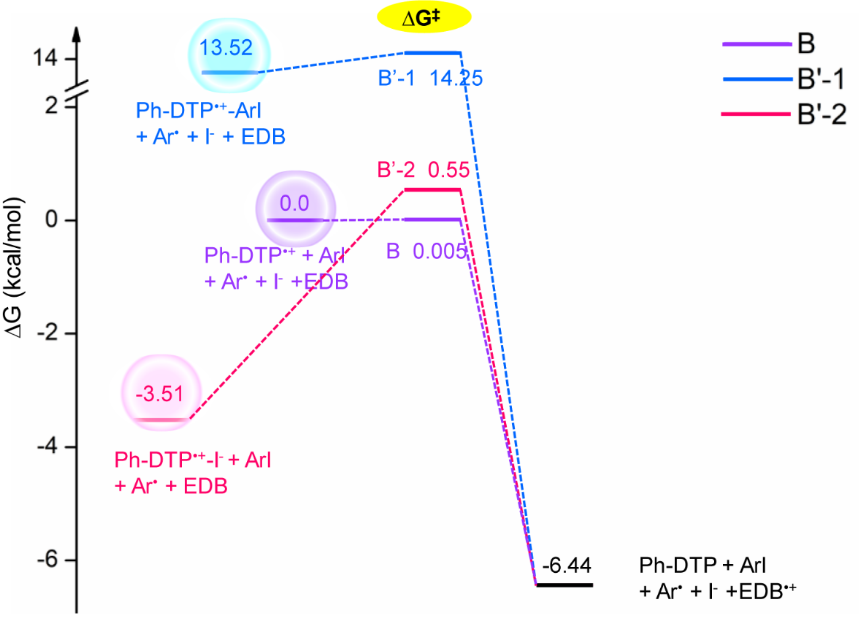

Fig. S2 Energy profiles of Ph-DTP$^{\bullet+}$/EDB/I^{-}/ArI/Ar$^{\bullet}$ following B, B'-1 and B'-2 deactivation paths.

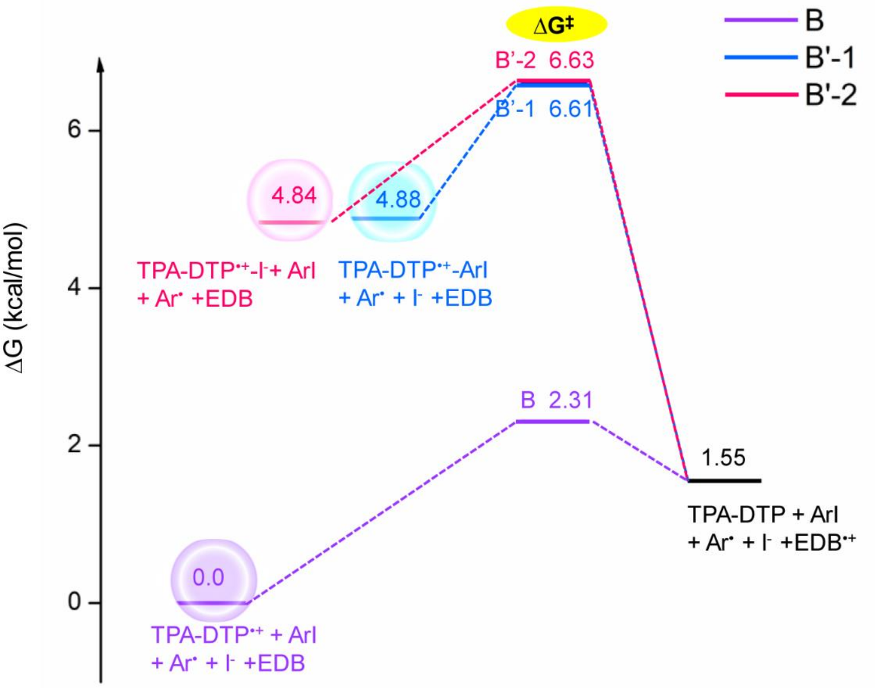

Fig. S3 Energy profiles of TPA-DTP$^{\bullet+}$/EDB/I^{-}/ArI/Ar$^{\bullet}$ following B, B'-1 and B'-2 deactivation paths.

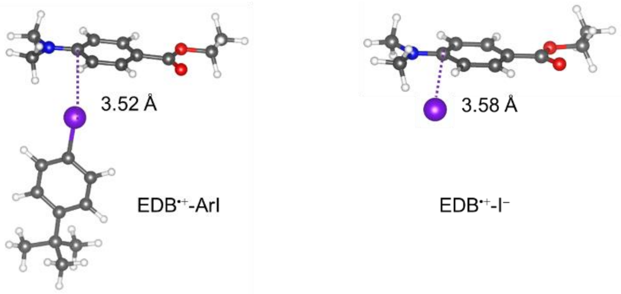

Fig. S4 Stable structures of radical cation complexes of type $EDB^{\bullet+}$-ArI and $EDB^{\bullet+}$-I^{-}.

After paths B, B’-1 and B’-2 take place, 10 different deactivation reactions can potentially follow to regenerate EDB and ArI/Ar_2I^+, namely B1 to B10.

Path B1

B1-a. $EDB^{\bullet+} + Ar^{\bullet} \rightarrow EDB + Ar^{+}$;

B1-b. $Ar^{+} + ArI \rightarrow Ar_2I^{+}$

In path B1-a, $\Delta_r G^{\theta}$ is the DFT calculated free energy with the value of 11.9 kcal/mol. The radius of $EDB^{\bullet+}$ is 6.872 Å.

$$\lambda_0 = 95\left(\frac{1}{2r_{EDB^{\bullet+}}} + \frac{1}{2r_{Ar^{\bullet}}} - \frac{1}{r_{EDB^{\bullet+}}+r_{Ar^{\bullet}}}\right)$$

= 8.93 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

= 2.23 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

= 12.15 kcal/mol

$$\mu = \frac{M_{EDB^{\bullet+}} M_{Ar^{\bullet}}}{M_{EDB^{\bullet+}}+M_{Ar^{\bullet}}}$$

= 78.74 g mol^{-1}

$$Z = N_A\sqrt{\frac{8\pi RT}{\mu}}\,(r_{EDB^{\bullet+}} + r_{Ar^{\bullet}})^2$$

= 7.07 ×10^{11} $M^{-1}s^{-1}$

$$k_{\mathrm{B1}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 8.76\times10^{2}\ \mathrm{M^{-1}s^{-1}}$

$R_{\mathrm{B1}} = k_{\mathrm{B1}}\,[\mathrm{EDB}^{\bullet+}][\mathrm{Ar}^{\bullet}]$

The concentration of $\mathrm{EDB}^{\bullet+}$ cannot be directly detected in electrochemical measurements. Therefore, about 10% of termination is considered here, such that a low concentration of 0.00513 M is used for $[\mathrm{EDB}^{\bullet+}]$.

$R_{\mathrm{B1}} = 2.08\times10^{-7}\ \mathrm{Ms^{-1}}$

R/R_{t} (Ph-DTP) = 10

Path B2

$\mathrm{EDB}^{\bullet+} + \mathrm{Ar}^{\bullet} + \mathrm{ArI} \rightarrow \mathrm{EDB} + \mathrm{Ar_2I^{+}}$

$$r_{\mathrm{eff}} = \frac{\left(2r_{\mathrm{Ar_2I^+}} - r_{\mathrm{ArI}}\right)r_{\mathrm{ArI}}}{r_{\mathrm{Ar_2I^+}}}$$

$= 7.371$ Å

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{EDB}^{\bullet+}}} + \frac{1}{2r_{\mathrm{eff}}} - \frac{1}{r_{\mathrm{EDB}^{\bullet+}} + r_{\mathrm{eff}}}\right)$$

$= 6.69$ kcal/mol

$\Delta_{\mathrm{r}}G^{\theta}$ is the DFT calculated free energy with the value of –25.76 kcal/mol, while D_{B} and D_{p} are the same as the ones shown in the Act-1 reaction.

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + \left(\sqrt{D_{\mathrm{B}}} - \sqrt{D_{\mathrm{p}}}\right)^2}{4}$$

$= 1.81$ kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta} - D_{\mathrm{p}}}{4\Delta G_0^{\ddagger}}\right)^2$$

$= 12.97$ kcal/mol

$$Z = N_{\mathrm{A}}^2 8\pi^2\sqrt{\frac{2RT}{\pi}}\left[\left(\frac{m_{\mathrm{A}}+m_{\mathrm{B}}}{m_{\mathrm{A}}m_{\mathrm{B}}}\right)^{\frac{1}{2}} + \left(\frac{m_{\mathrm{B}}+m_{\mathrm{C}}}{m_{\mathrm{B}}m_{\mathrm{C}}}\right)^{\frac{1}{2}}\right] d_{\mathrm{A\leftrightarrow B}}^2 d_{\mathrm{B\leftrightarrow C}}^2 \delta$$

Here, we define A = $\mathrm{EDB}^{\bullet+}$, B = $\mathrm{Ar}^{\bullet}$, and C = ArI, such that $m_{\mathrm{A}} = 0.193\ \mathrm{kgmol^{-1}}$, $m_{\mathrm{B}} = 0.133$ kgmol^{-}

^{1}, and m_C = 0.26 kgmol^{-1}. With these values and their corresponding radii, Z can be obtained.

$Z = 3.34\times10^{11}$ M^{-2}s^{-1}

$$k_{B2} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 1.04\times10^{2}$ M^{-2}s^{-1}

$R_{B2} = k_{B2}\,[\mathrm{EDB}^{\bullet+}][\mathrm{Ar}^{\bullet}][\mathrm{ArI}]$

$= 4.54\times10^{-11}$ Ms^{-1}

$R/R_t = 2.16\times10^{-3}$

Path B3

$\mathrm{EDB}^{\bullet+}\text{-ArI} + \mathrm{Ar}^{\bullet} \rightarrow \mathrm{EDB} + \mathrm{Ar_2I}^{+}$

$\Delta_r G^{\theta}$ is the DFT calculated free energy with the value of –30.82 kcal/mol, and D_B is the bond dissociation energy of EDB$^{\bullet+}$-ArI with the value of 3.3 kcal/mol. The radius of EDB$^{\bullet+}$-ArI is 8.748 Å.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{EDB}^{\bullet+}\text{-ArI}}} + \frac{1}{2r_{\mathrm{Ar}^{\bullet}}} - \frac{1}{r_{\mathrm{EDB}^{\bullet+}\text{-ArI}}+r_{\mathrm{Ar}^{\bullet}}}\right)$$

$= 8.6$ kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_B}{4}$$

$= 2.975$ kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$= 7.52$ kcal/mol

$$\mu = \frac{M_{\mathrm{EDB}^{\bullet+}\text{-ArI}}M_{\mathrm{Ar}^{\bullet}}}{M_{\mathrm{EDB}^{\bullet+}\text{-ArI}}+M_{\mathrm{Ar}^{\bullet}}}$$

$= 102.81$ g mol^{-1}

$$Z = N_A\sqrt{\frac{8\pi RT}{\mu}}\,(r_{\mathrm{EDB}^{\bullet+}\text{-ArI}} + r_{\mathrm{Ar}^{\bullet}})^2$$

$= 8.38\times10^{11}$ M^{-1}s^{-1}

$$k_{B3} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 2.57\times10^{6}\ \mathrm{M^{-1}s^{-1}}$

The calculation of the concentration of $\mathrm{EDB^{\bullet+}}$-ArI:

$\mathrm{EDB^{\bullet+} + ArI \leftrightarrow EDB^{\bullet+}\text{-}ArI}$ (RB3-M)

Reaction equilibrium constant k_f of RB3-M:

$$k_f = e^{-\frac{\Delta_r G^{\theta}(\text{RB3-M})}{RT}} = \frac{[\mathrm{EDB^{\bullet+}\text{-}ArI}]}{[\mathrm{EDB^{\bullet+}}][\mathrm{ArI}]}$$

$\Delta_r G^{\theta}{}_{(\text{RB3-M})}$ is the DFT calculated free energy with the value of 5.06 kcal/mol.

$k_f = \exp(-5.06\mathrm{kcal\ mol^{-1}}/(1.987\ \mathrm{calmol^{-1}K^{-1}}\times 298.15\ \mathrm{K})) = 1.96\times10^{-4}$

Then, the concentration of $\mathrm{EDB^{\bullet+}}$-ArI can be obtained.

$[\mathrm{EDB^{\bullet+}\text{-}ArI}] = 1.85\times10^{-9}\ \mathrm{M}$

$R_{\mathrm{B3}} = k_{\mathrm{B3}}\ [\mathrm{EDB^{\bullet+}\text{-}ArI}][\mathrm{Ar^{\bullet}}]$

$= 2.2\times10^{-10}\ \mathrm{Ms^{-1}}$

$R/R_t = 0.01$

Path B4

B4-a. $\mathrm{EDB^{\bullet+}\text{-}ArI + Ar^{\bullet} \rightarrow EDB + ArI + Ar^{+}}$;

B4-b. $\mathrm{Ar^{+} + ArI \rightarrow Ar_2I^{+}}$

In path B4-a, $\Delta_r G^{\theta}$ is the DFT calculated free energy with the value of 6.84 kcal/mol. λ_0, D_{B}, $\Delta G_0^{\ddagger}$, Z and μ are the same as the ones shown in path B3.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$= 7.39$ kcal/mol

$$k_{\mathrm{B4}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 3.2\times10^{6}\ \mathrm{M^{-1}s^{-1}}$

$R_{\mathrm{B4}} = k_{\mathrm{B4}}\ [\mathrm{EDB^{\cdot+}\text{-}ArI}][\mathrm{Ar^{\bullet}}]$

$= 2.74\times10^{-10}\ \mathrm{Ms^{-1}}$

$R/R_t = 1.3\times10^{-2}$

Path B5

B5-a. $\mathrm{EDB^{\bullet+}\text{-}ArI + Ar^{\bullet} \rightarrow EDB\text{-}ArI + Ar^{+}}$

B5-b. $\mathrm{EDB\text{-}ArI \rightarrow EDB + ArI}$

B5-c. $\mathrm{Ar^{+} + ArI \rightarrow Ar_2I^{+}}$

In reaction B5-a, the DFT calculated free energy $\Delta_r G^{\theta} = 9.23$ kcal/mol. λ_0, Z and μ are the same as the ones shown in path B3.

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

= 2.15 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

= 9.24 kcal/mol

$$k_{B5} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 1.41\times10^{5}\ \mathrm{M^{-1}s^{-1}}$

$R_{B5} = k_{B5}\,[\mathrm{EDB^{\bullet+}\text{-}ArI}][\mathrm{Ar^{\bullet}}]$

$= 1.21\times10^{-11}\ \mathrm{Ms^{-1}}$

$R/R_t = 5.76\times10^{-4}$

Path B6

B6-a. $\mathrm{EDB^{\bullet+} + Ar^{\bullet} \rightarrow EDB + Ar^{+}}$

B6-b. $\mathrm{Ar^{+} + I^{-} \rightarrow ArI}$

In reaction B6-a, all the relevant parameters are the same as the ones shown in path B1-a.

Path B7

$\mathrm{EDB^{\bullet+} + Ar^{\bullet} + I^{-} \rightarrow EDB + ArI}$

The DFT calculated free energy $\Delta_r G^{\theta} = -51.06$ kcal/mol, while D_B and D_p are the same as the ones shown in the Act-2 reaction. r_{eff} is as shown in Table S1.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{EDB}^{\bullet+}}} + \frac{1}{2r_{\mathrm{eff}}} - \frac{1}{r_{\mathrm{EDB}^{\bullet+}}+r_{\mathrm{eff}}}\right)$$

= 12.05 kcal/mol

$$G_0^{\ddagger} = \frac{\lambda_0 + \left(\sqrt{D_{\mathrm{B}}} - \sqrt{D_{\mathrm{p}}}\right)^2}{4}$$

= 8.69 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta} - D_{\mathrm{p}}}{4\Delta G_0^{\ddagger}}\right)^2$$

= 2.24 kcal/mol

$$Z = N_{\mathrm{A}}^2 8\pi^2\sqrt{\frac{2RT}{\pi}}\left[\left(\frac{m_{\mathrm{A}}+m_{\mathrm{B}}}{m_{\mathrm{A}}m_{\mathrm{B}}}\right)^{\frac{1}{2}} + \left(\frac{m_{\mathrm{B}}+m_{\mathrm{C}}}{m_{\mathrm{B}}m_{\mathrm{C}}}\right)^{\frac{1}{2}}\right] d_{\mathrm{A}\leftrightarrow\mathrm{B}}^2 d_{\mathrm{B}\leftrightarrow\mathrm{C}}^2\delta$$

Here we define A = $\mathrm{EDB}^{\bullet+}$, B = $\mathrm{Ar}^{\bullet}$ and C = I^{-}.

$Z = 1.47\times10^{11}\ \mathrm{M}^{-2}\mathrm{s}^{-1}$

$$k_{\mathrm{B7}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 3.35\times10^{9}\ \mathrm{M}^{-2}\mathrm{s}^{-1}$

$R_{\mathrm{B7}} = k_{\mathrm{B7}}\,[\mathrm{EDB}^{\bullet+}][\mathrm{Ar}^{\bullet}][\mathrm{I}^{-}]$

$= 1.46\times10^{-4}\ \mathrm{Ms}^{-1}$

$R/R_{\mathrm{t}} = 6.96\times10^{3}$

Path B8

$\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^{-} + \mathrm{Ar}^{\bullet} \rightarrow \mathrm{EDB} + \mathrm{ArI}$

$\Delta_{\mathrm{r}}G^{\theta}$ is the DFT calculated free energy with the value of –54.53 kcal/mol, and D_{B} is the bond dissociation energy of $\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^{-}$ with the value of 2.356 kcal/mol. The radius of $\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^{-}$ is 7.009 Å.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^{-}}} + \frac{1}{2r_{\mathrm{Ar}}} - \frac{1}{r_{\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^{-}}+r_{\mathrm{Ar}}}\right)$$

= 8.89 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\mathrm{B}}}{4}$$

= 2.81 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}} G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$= 41.68$ kcal/mol

$$\mu = \frac{M_{\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-} M_{\mathrm{Ar}^{\bullet}}}{M_{\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-} + M_{\mathrm{Ar}^{\bullet}}}$$

$= 93.95$ g mol^{-1}

$$Z = N_{\mathrm{A}} \sqrt{\frac{8\pi RT}{\mu}}\,(r_{\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-} + r_{\mathrm{Ar}^{\bullet}})^2$$

$= 6.63 \times 10^{11}$ M^{-1}s^{-1}

$$k_{\mathrm{B8}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 1.85\times10^{-19}$ M^{-1}s^{-1}

The calculation of the concentration of $\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-$:

$\mathrm{EDB}^{\bullet+} + \mathrm{I}^- \leftrightarrow \mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-$ (RB8-M)

Reaction equilibrium constant k_f of RB3-M:

$$k_f = e^{-\frac{\Delta_{\mathrm{r}} G^{\theta}(\mathrm{RB8\text{-}M})}{RT}} = \frac{[\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-]}{[\mathrm{EDB}^{\bullet+}][\mathrm{I}^-]}$$

$\Delta_{\mathrm{r}}G^{\theta}{}_{(\mathrm{RB8\text{-}M})}$ is the DFT calculated free energy with the value of 3.47 kcal/mol.

$k_f = \exp(-3.47 \text{ kcal mol}^{-1}/(1.987 \text{ calmol}^{-1}\text{K}^{-1}\times 298.15 \text{ K})) = 2.85\times10^{-3}$

Then the concentration of $\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-$ can be obtained.

$[\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-] = 2.85\times10^{-3} \times 0.00513 \times 1.84\times10^{-4} = 2.69\times10^{-9}$ M

$R_{\mathrm{B8}} = k_{\mathrm{B8}}\, [\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^-][\mathrm{Ar}^{\bullet}]$

$= 2.3\times10^{-35}$ Ms^{-1}

$R/R_{\mathrm{t}} = 1.1\times10^{-27}$

Path B9

B9-a. $\mathrm{EDB}^{\bullet+}\text{-}\mathrm{I}^- + \mathrm{Ar}^{\bullet} \rightarrow \mathrm{EDB} + \mathrm{I}^- + \mathrm{Ar}^+$

B9-b. $\mathrm{Ar}^+ + \mathrm{I}^- \rightarrow \mathrm{ArI}$

In path B9-a, $\Delta_{\mathrm{r}}G^{\theta}$ is the DFT calculated free energy with the value of 8.43 kcal/mol, while λ_0, D_{B},

$\Delta G_0^{\ddagger}$, Z and μ are the same as the ones shown in path B8.

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

= 8.61 kcal/mol

$$k_{B9} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 3.26\times10^{5}\ M^{-1}s^{-1}$

$R_{B9} = k_{B9}\ [EDB^{\cdot+}\text{-}I^{-}][Ar^{\bullet}]$

$= 4.05\times10^{-11}\ Ms^{-1}$

$R/R_t = 1.93\times10^{-3}$

Path B10

B10-a. $EDB^{\bullet+}\text{-}I^{-} + Ar^{\bullet} \rightarrow EDB\text{-}I^{-} + Ar^{+}$

B10-b. $EDB\text{-}I^{-} \rightarrow EDB + I^{-}$

B10-c. $Ar^{+} + I^{-} \rightarrow ArI$

In reaction B10-a, the DFT calculated free energy $\Delta_r G^{\theta}$ = 9.604 kcal/mol. λ_0, Z and μ are the same as the ones shown in path B8.

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

= 2.22 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

= 9.62 kcal/mol

$$k_{B10} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 5.88\times10^{4}\ M^{-1}s^{-1}$

$R_{B10} = k_{B10}\ [EDB^{\cdot+}\text{-}ArI][Ar^{\bullet}]$

$= 7.31\times10^{-12}\ Ms^{-1}$

$R/R_t = 3.48\times10^{-4}$

Path C

C-a. $Ar^{\bullet} + EDB \rightarrow ArH + EDB^{\bullet}_{(-H)}$

C-b. $EDB^{\bullet}_{(-H)} + DTP^{\bullet+} \rightarrow EDB^{+}_{(-H)} + DTP$

C-c. $EDB^{+}_{(-H)} + ArH \rightarrow EDB + Ar^{+}$

C-d. $Ar^{+} + ArI \rightarrow Ar_2I^{+}$

In reaction C-a, the DFT calculated free energy $\Delta_r G^{\theta}$ = –3.01 kcal/mol, while D_B is the bond dissociation energy of $EDB \rightarrow EDB_{(-H)}^{\bullet} + H^{\bullet}$ with the value of 120.05 kcal/mol. μ is the same as the one shown in path B1.

$$\lambda_0 = 95\left(\frac{1}{2r_{EDB}} + \frac{1}{2r_{Ar^{\bullet}}} - \frac{1}{r_{EDB}+r_{Ar^{\bullet}}}\right)$$

= 8.92 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_B}{4}$$

= 32.24 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

= 30.75 kcal/mol

$Z = 7.12 \times 10^{11}\ M^{-1}s^{-1}$

$$k_{C\text{-}a} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 2.04\times10^{-11}\ M^{-1}s^{-1}$

$R_{C\text{-}a} = k_{C\text{-}a}\,[EDB][Ar^{\bullet}]$

$= 4.83\times10^{-20}\ Ms^{-1}$

$R/R_t = 2.3\times10^{-12}$

In reaction C-b, the DFT calculated free energy $\Delta_r G^{\theta}$ is 2.34 kcal/mol for the Ph-DTP case and 10.33 kcal/mol for the TPA-DTP case. The radius of $EDB^{\bullet}_{(-H)}$ is 7 Å.

$$\lambda_0 = 95\left(\frac{1}{2r_{EDB^{\bullet}(-H)}} + \frac{1}{2r_{DTP^{\bullet+}}} - \frac{1}{r_{EDB^{\bullet}(-H)}+r_{DTP^{\bullet+}}}\right)$$

λ_0 (Ph-DTP) = 6.03 kcal/mol

λ_0 (TPA-DTP) = 5.66 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 1.51 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 1.415 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 2.91 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 11.29 kcal/mol

$$\mu = \frac{M_{\mathrm{EDB}^{\bullet}{}_{(\text{-H})}} M_{\mathrm{DTP}^{\bullet +}}}{M_{\mathrm{EDB}^{\bullet}{}_{(\text{-H})}} + M_{\mathrm{DTP}^{\bullet +}}}$$

μ (Ph-DTP) = 133.67 g mol^{-1}

μ (TPA-DTP) = 153.84 g mol^{-1}

$$Z = N_{\mathrm{A}} \sqrt{\frac{8\pi RT}{\mu}} \left(r_{\mathrm{EDB}^{\bullet}{}_{(\text{-H})}} + r_{\mathrm{DTP}^{\bullet +}}\right)^2$$

Z (Ph-DTP) = 1.12×10^{12} M^{-1}s^{-1}

Z (TPA-DTP) = 1.68×10^{12} M^{-1}s^{-1}

$$k_{\text{C-b}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$k_{\text{C-b}}$ (Ph-DTP) = 8.24×10^{9} M^{-1}s^{-1}

$k_{\text{C-b}}$ (TPA-DTP) = 8.89×10^{3} M^{-1}s^{-1}

$R_{\text{C-b}} = k_{\text{C-b}}\,[\mathrm{EDB}^{\bullet}{}_{(\text{-H})}][\mathrm{DTP}^{\bullet +}]$

$R_{\text{C-b}}$ (Ph-DTP) = 7.78×10^{2} Ms^{-1}

$R_{\text{C-b}}$ (TPA-DTP) = 8.39×10^{-4} Ms^{-1}

R/R_{t} (Ph-DTP) = 3.7×10^{10}

R/R_{t} (TPA-DTP) = 4×10^{4}

From observing the various reaction steps involved in path C, the high bond dissociation energy of EDB appears to render a challenge towards their feasibility. Besides, the calculated high activation barriers indicate that path C is in fact difficult to carry out.

Table S3. Calculated activation barriers of each proposed deactivation path, B, B' and B1–B10

Path		$\Delta G_1^{\ddagger}$ (kcal/mol)	Path	$\Delta G_2^{\ddagger}$ (kcal/mol)
B	Ph-DTP	0.005	B1	12.15
	TPA-DTP	2.31	B2	12.97
B'-1	Ph-DTP	0.73	B3	7.52
	TPA-DTP	1.73	B4	7.39
B'-2	Ph-DTP	4.06	B5	9.24
	TPA-DTP	1.79	B6	12.15
			B7	2.24
			B8	41.68
			B9	8.61
			B10	9.62

Note S2.4 Deactivation processes in the PC–EDB system

Experimental studies on the polymerization kinetics have found inconspicuous photolysis conversion in the DTPs-EDB system, while its electron transfer quantum yield of about 0.25[17] claims that back electron transfer would occur during the interaction. This means that although the Act-3 process has a rather high activation barrier (Table 1), the $DTP^{\bullet-}$ and $EDB^{\bullet+}$ species still have a chance to be generated. Herein, the deactivation mechanisms involved among the co-existing components $DTP^{\bullet-}/EDB^{\bullet+}/Ar_2I^+$ are investigated. Three possible mechanisms can be found, as denoted by paths D, D' and E. The relevant activation energy and rate constant in each path are shown in Table S4 and Table S5, and their energy profiles are shown in Fig. S5-6.

Path D

D-a. $DTP^{\bullet-} + EDB^{\bullet+} \rightarrow DTP\text{-}H^{\bullet} + EDB^{\bullet}(-H)$

D-b. $\text{DTP-H}^{\bullet} + \text{Ar}_2\text{I}^{+} \rightarrow \text{DTP} + \text{H}^{+} + \text{ArI} + \text{Ar}^{\bullet}$

D-c. $\text{EDB}^{\bullet}(\text{–H}) + \text{H}^{+} + \text{Ar}^{\bullet} \rightarrow \text{EDB} + \text{Ar}^{+}$

D-d. $\text{Ar}^{+} + \text{ArI} \rightarrow \text{Ar}_2\text{I}^{+}$

In reaction D-a, the DFT calculated free energy $\Delta_{\text{r}}G^{\theta}$ is 14.13 kcal/mol for the Ph-DTP case and 37.26 kcal/mol for the TPA-DTP case. D_{B} is the bond dissociation energy of $\text{EDB}^{\bullet+} \rightarrow \text{EDB}_{(\text{-H})}^{\bullet} + \text{H}^{+}$ with the value of 177.08 kcal/mol. Such a high value means that it is hard to obtain $\text{EDB}_{(\text{-H})}^{\bullet}$ without the intervention of a strong external stimulus.

The radii of $\text{DTP}^{\bullet-}$ are 9.591 and 14.06 Å for Ph-DTP$^{\bullet-}$ and TPA-DTP$^{\bullet-}$, respectively.

$$\lambda_0 = 95\left(\frac{1}{2r_{\text{EDB}^{\bullet+}}} + \frac{1}{2r_{\text{DTP}^{\bullet-}}} - \frac{1}{r_{\text{EDB}^{\bullet+}}+r_{\text{DTP}^{\bullet-}}}\right)$$

λ_0 (Ph-DTP) = 6.09 kcal/mol

λ_0 (TPA-DTP) = 5.75 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\text{B}}}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 45.79 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 45.71 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\text{r}}G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 53.13 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 66.24 kcal/mol

μ is the same as the one shown in path B.

$$Z = N_{\text{A}}\sqrt{\frac{8\pi RT}{\mu}}\left(r_{\text{EDB}^{\bullet+}} + r_{\text{DTP}^{\bullet-}}\right)^2$$

Z (Ph-DTP) = 1.11×10^{12} $\text{M}^{-1}\text{s}^{-1}$

Z (TPA-DTP) = 1.68×10^{12} $\text{M}^{-1}\text{s}^{-1}$

$$k_{\text{D-a}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$K_{\text{D-a}}$ (Ph-DTP) = 1.25×10^{-27} $\text{M}^{-1}\text{s}^{-1}$

$K_{\text{D-a}}$ (TPA-DTP) = 4.64×10^{-37} $\text{M}^{-1}\text{s}^{-1}$

$R_{\text{D-a}} = k_{\text{D-a}}\,[\text{EDB}^{\bullet+}][\text{DTP}^{\bullet-}]$

Here, the concentration of $\mathrm{DTP}^{\bullet-}$ is the same as that of $\mathrm{DTP}^{\bullet+}$.

$R_{\text{D-a}}$ (Ph-DTP) = 1.18×10^{-34} $\mathrm{Ms^{-1}}$

$R_{\text{D-a}}$ (TPA-DTP) = 4.38×10^{-44} $\mathrm{Ms^{-1}}$

R/R_{t} (Ph-DTP) = 5.62×10^{-27}

R/R_{t} (TPA-DTP) = 2.09×10^{-36}

In reaction D-b, the DFT calculated free energy $\Delta_{\mathrm{r}}G^{\theta}$ is 108.58 kcal/mol for the Ph-DTP case and 84.19 kcal/mol for the TPA-DTP case. D_{B} is the bond dissociation energy with values of 58.58 kcal/mol (Ph-DTP-$\mathrm{H}^{\bullet}$), 17.22 kcal/mol (TPA-DTP-$\mathrm{H}^{\bullet}$) and 2.75 kcal/mol ($\mathrm{Ar_2I^+}$). The radii of DTP-$\mathrm{H}^{\bullet}$ are 9.586 and 14.017 Å for Ph-DTP-$\mathrm{H}^{\bullet}$ and TPA-DTP-$\mathrm{H}^{\bullet}$, respectively.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{Ar_2I^+}}} + \frac{1}{2r_{\text{DTP-H}^{\bullet}}} - \frac{1}{r_{\mathrm{Ar_2I^+}}+r_{\text{DTP-H}^{\bullet}}}\right)$$

λ_0 (Ph-DTP) = 5.47 kcal/mol

λ_0 (TPA-DTP) = 4.99 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\mathrm{B}}}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 16.7 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 6.24 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 115.11 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 119.33 kcal/mol

$$\mu = \frac{M_{\text{DTP-H}^{\bullet}} M_{\mathrm{Ar_2I^+}}}{M_{\text{DTP-H}^{\bullet}} + M_{\mathrm{Ar_2I^+}}}$$

μ (Ph-DTP) = 207.81 g $\mathrm{mol^{-1}}$

μ (TPA-DTP) = 260.77 g $\mathrm{mol^{-1}}$

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\left(r_{\mathrm{Ar_2I^+}} + r_{\text{DTP-H}^{\bullet}}\right)^2$$

Z (Ph-DTP) = 1.02×10^{12} $\mathrm{M^{-1}s^{-1}}$

Z (TPA-DTP) = 1.43×10^{12} $\mathrm{M^{-1}s^{-1}}$

$$k_{\text{D-b}} = Z\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$K_{\text{D-b}}$ (Ph-DTP) = 4.2×10^{-73} $\text{M}^{-1}\text{s}^{-1}$

$K_{\text{D-b}}$ (TPA-DTP) = 4.75×10^{-76} $\text{M}^{-1}\text{s}^{-1}$

To obtain the concentration of DTP-H$^{\bullet}$, the reaction equilibrium constant k_f of reaction D-a should be calculated.

$$k_f = e^{-\frac{\Delta_r G^{\theta}(\text{D-a})}{RT}} = \frac{[\text{EDB}^{\bullet}(\text{-H})][\text{DTP-H}^{\bullet}]}{[\text{EDB}^{\bullet+}][\text{DTP}^{\bullet-}]}$$

k_f (Ph-DTP) = 4.38×10^{-11}

k_f (TPA-DTP) = 4.85×10^{-28}

[Ph-DTP-H$^{\bullet}$] = 8.06×10^{-16} M

[TPA-DTP-H$^{\bullet}$] = 8.92×10^{-33} M

$R_{\text{D-b}} = k_{\text{D-b}}\,[\text{DTP-H}^{\bullet}][\text{Ar}_2\text{I}^{+}]$

$R_{\text{D-b}}$ (Ph-DTP) = 6.23×10^{-90} Ms^{-1}

$R_{\text{D-b}}$ (TPA-DTP) = 7.8×10^{-110} Ms^{-1}

R/R_{t} (Ph-DTP) = 2.97×10^{-82}

R/R_{t} (TPA-DTP) = 3.71×10^{-102}

In reaction D-c, the DFT calculated free energy $\Delta_r G^{\theta}$ is –144.31 kcal/mol, while D_{B} is the same as the one in reaction D-a. r_{eff} can be obtained by $\frac{(2r_{\text{Ar}^{\bullet}} - r_{\text{H}})r_{\text{H}}}{r_{\text{Ar}^{\bullet}}}$, giving the value of 2.088 Å.

$$\lambda_0 = 95\left(\frac{1}{2r_{\text{EDB}^{\bullet}(\text{-H})}} + \frac{1}{2r_{\text{eff}}} - \frac{1}{r_{\text{EDB}^{\bullet}(\text{-H})}+r_{\text{eff}}}\right)$$

$$= 19.08 \text{ kcal/mol}$$

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\text{B}}}{4}$$

$$= 49.04 \text{ kcal/mol}$$

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$$= 3.43 \text{ kcal/mol}$$

$$Z = N_{\text{A}}^2 8\pi^2 \sqrt{\frac{2RT}{\pi}}\left[\left(\frac{m_{\text{A}}+m_{\text{B}}}{m_{\text{A}}m_{\text{B}}}\right)^{\frac{1}{2}} + \left(\frac{m_{\text{B}}+m_{\text{C}}}{m_{\text{B}}m_{\text{C}}}\right)^{\frac{1}{2}}\right] d_{\text{A}\leftrightarrow\text{B}}^2 d_{\text{B}\leftrightarrow\text{C}}^2 \delta$$

Here, we define A = EDB$^{\bullet}$(–H), B = H^{+} and C = Ar$^{\bullet}$.

$Z = 6.83\times10^{11}$ M^{-2}s^{-1}

$$k_{\text{D-c}} = Z \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

$= 2.1\times10^{9}$ M^{-2}s^{-1}

Above all, the bond dissociation energy of EDB$^{\bullet+}$ of 177.08 kcal/mol and high barriers of 53.13 (Ph-DTP$^{\bullet-}$) and 66.24 kcal/mol (TPA-DTP$^{\bullet-}$) indicate that path D is hard to carry out.

Path D'

DTP$^{\bullet-}$ + EDB$^{\bullet+}$ → DTP + EDB

In reaction D', the DFT calculated free energy $\Delta_r G^{\theta}$ is –59.27 kcal/mol for the Ph-DTP case and –60.53 kcal/mol for the TPA-DTP case. λ_0 and Z are same as the one shown in path D-a.

$$\Delta G_0^{\ddagger} = \frac{\lambda_0}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 1.52 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 1.44 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 115.91 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 130.7 kcal/mol

Above all, the high barriers of 115.91 (Ph-DTP$^{\bullet-}$) and 130.7 kcal/mol (TPA-DTP$^{\bullet-}$) indicate that path D' is hard to carry out. Then the calculation for $K_{\text{D'}}$ and $R_{\text{D'}}$ has no significance.

Path E

DTP$^{\bullet-}$ + Ar_2I^+ → DTP + Ar$^{\bullet}$ + ArI

In reaction E, DTP$^{\bullet-}$ first reacts with Ar_2I^+ to give birth to DTP, ArI and Ar$^{\bullet}$ species. The co-existing EDB$^{\bullet+}$/Ar$^{\bullet}$/ArI components then undergo reduction reactions E1–E5 to regenerate EDB and Ar_2I^+. It should be noted that paths E1–E5 are the same as paths B1–B5.

In the first step of reaction E, the DFT calculated free energy $\Delta_r G^{\theta}$is –33.51 kcal/mol for the Ph-DTP case and –34.76 kcal/mol for the TPA-DTP case. D_B and μ are the same as the ones in reaction Act-1.

$$\lambda_0 = 95\left(\frac{1}{2r_{\mathrm{Ar_2I^+}}} + \frac{1}{2r_{\mathrm{DTP^{\bullet-}}}} - \frac{1}{r_{\mathrm{Ar_2I^+}}+r_{\mathrm{DTP^{\bullet-}}}}\right)$$

λ_0 (Ph-DTP) = 5.47 kcal/mol

λ_0 (TPA-DTP) = 4.99 kcal/mol

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + D_{\mathrm{B}}}{4}$$

$\Delta G_0^{\ddagger}$ (Ph-DTP) = 2.055 kcal/mol

$\Delta G_0^{\ddagger}$ (TPA-DTP) = 1.935 kcal/mol

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_{\mathrm{r}}G^{\theta}}{4\Delta G_0^{\ddagger}}\right)^2$$

$\Delta G^{\ddagger}$ (Ph-DTP) = 19.45 kcal/mol

$\Delta G^{\ddagger}$ (TPA-DTP) = 23.58 kcal/mol

$$Z = N_{\mathrm{A}}\sqrt{\frac{8\pi RT}{\mu}}\left(r_{\mathrm{Ar_2I^+}} + r_{\mathrm{DTP^{\bullet-}}}\right)^2$$

Z (Ph-DTP) = 1.025×10^{12} $\mathrm{M^{-1}s^{-1}}$

Z (TPA-DTP) = 1.44×10^{12} $\mathrm{M^{-1}s^{-1}}$

k_{E} (Ph-DTP) = 5.65×10^{-3} $\mathrm{M^{-1}s^{-1}}$

k_{E} (TPA-DTP) = 7.45×10^{-6} $\mathrm{M^{-1}s^{-1}}$

R_{E} (Ph-DTP) = 1.91×10^{-9} $\mathrm{Ms^{-1}}$

R_{E} (TPA-DTP) = 2.52×10^{-12} $\mathrm{Ms^{-1}}$

R/R_{t} (Ph-DTP) = 0.09

R/R_{t} (TPA-DTP) = 1.2×10^{-4}

Compared to path D and path D’, path E has a moderate activation barrier and can offer a more likely deactivation mechanism for the Act-3 activation process. However, its low R/R_{t} values indicate that the deactivation of $\mathrm{DTP^{\bullet-}}$ is in competition with the biradical termination reaction. This will inevitably lead to a poor efficiency to obtain required photopolymerization results.

Table S4. Calculated activation energies of proposed deactivation paths, D, D' and E.

Path		$\Delta G_1^{\ddagger}$ (kcal/mol)	Path		$\Delta G_2^{\ddagger}$ (kcal/mol)	$\Delta G_3^{\ddagger}$ (kcal/mol)
D	Ph-DTP	53.13			115.11	3.43
	TPA-DTP	66.24			119.33	3.43
D'	Ph-DTP	115.91				
	TPA-DTP	130.7				
E	Ph-DTP	19.45				
	TPA-DTP	23.58				
			E1	Ph-DTP	12.15	—
				TPA-DTP	12.15	—
			E2	Ph-DTP	12.97	—
				TPA-DTP	12.97	—
			E3	Ph-DTP	7.52	—
				TPA-DTP	7.52	—
			E4	Ph-DTP	7.39	—
				TPA-DTP	7.39	—
			E5	Ph-DTP	9.24	—
				TPA-DTP	9.24	—

Table S5. Calculated rate constants of proposed deactivation paths D and E.

Path		Reaction	Rate law	k ($M^{-1}s^{-1}$)	R (Ms^{-1})	R/R_t
Termination		$P_n^{\bullet} + P_n^{\bullet} \rightarrow P_n\text{-}P_n$	$R_t = k_t[P_n^{\bullet}][P_n^{\bullet}]$	10^7	2.1×10^{-8}	1
D	Ph-DTP	$DTP^{\bullet-} + EDB^{\bullet+} \rightarrow DTP\text{-}H^{\bullet} + EDB^{\bullet}(\text{-}H)$	$R_D = k_D[EDB^{\bullet+}][DTP^{\bullet-}]$	1.25×10^{-27}	1.18×10^{-34}	5.62×10^{-27}
		$DTP\text{-}H^{\bullet} + Ar_2I^+ \rightarrow DTP + H^+ + ArI + Ar^{\bullet}$				
	TPA-DTP	$EDB^{\bullet}(\text{-}H) + H^+ + Ar^{\bullet} \rightarrow EDB + Ar^+$		4.64×10^{-37}	4.38×10^{-44}	2.09×10^{-36}
		$Ar^+ + ArI \rightarrow Ar_2I^+$				
E	Ph-DTP	$DTP^{\bullet-} + Ar_2I^+ \rightarrow DTP + Ar^{\bullet} + ArI$	$R_E = k_E[DTP^{\bullet-}][Ar_2I^+]$	5.65×10^{-3}	1.91×10^{-9}	0.09
	TPA-DTP			7.45×10^{-6}	2.52×10^{-12}	1.2×10^{-4}

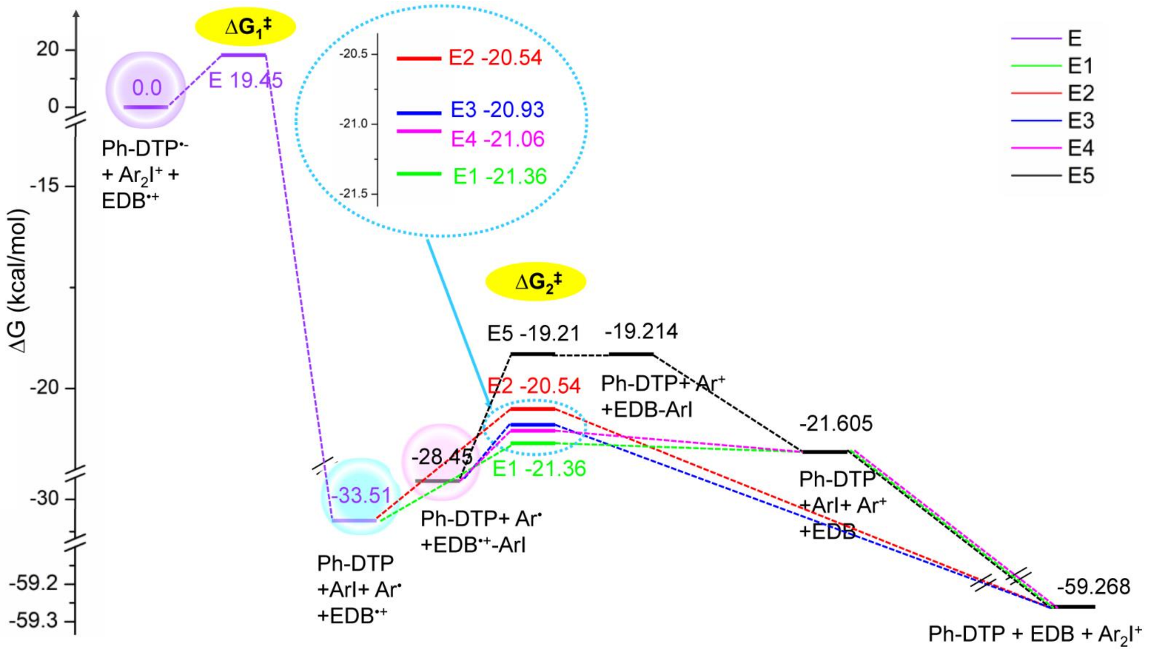

Fig. S5 Energy profiles of Ph-DTP$^{\bullet+}$/EDB/Ar$_2$I$^+$ following E-series deactivation paths.

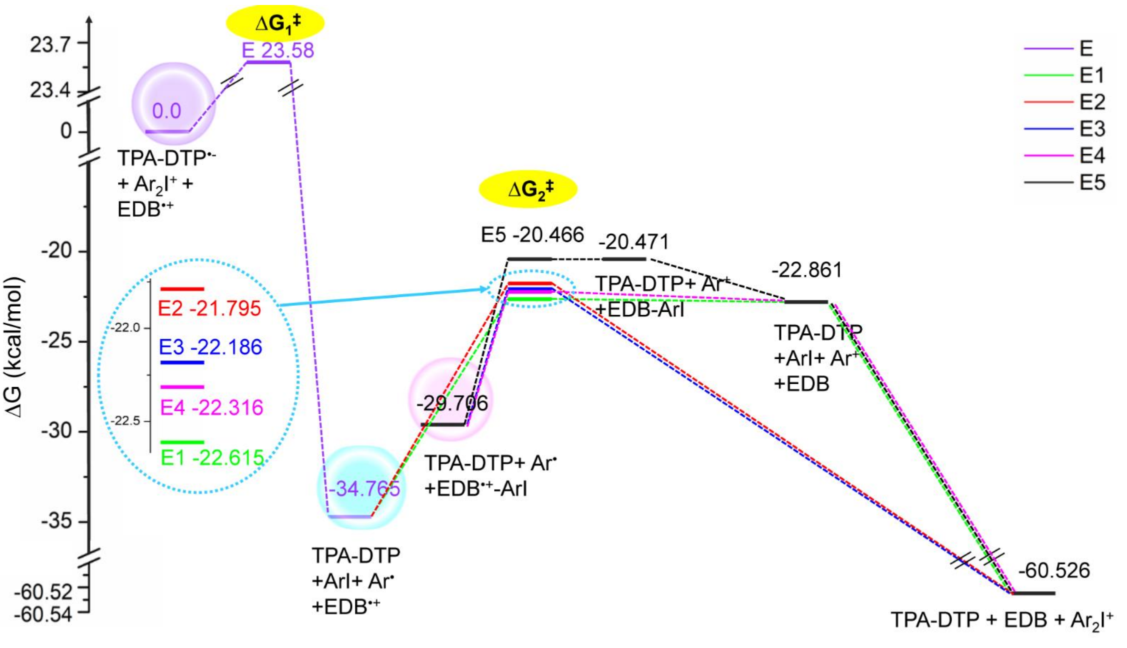

Fig. S6 Energy profiles of TPA-DTP$^{\bullet+}$/EDB/Ar$_2$I$^+$ following E-series deactivation paths.

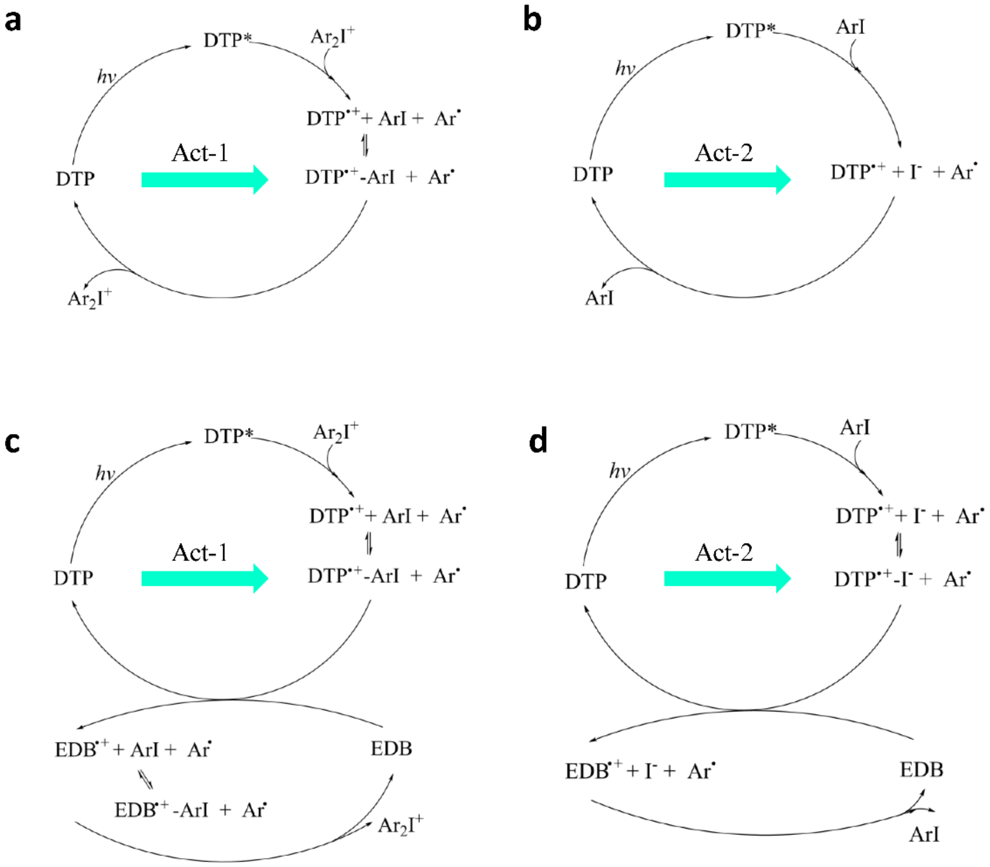

Fig. S7 The overall main mechanism in the photo-catalytic cycle for the (a) DTPs-Ar_2I^+ system following the Act-1 activation process and A1-A5 deactivation processes, (b) DTPs-ArI system following the Act-2 activation process and A6-A10 deactivation processes, (c) DTPs-Ar_2I^+-EDB system following the Act-1 activation process and B, B'-1, B1-B5 deactivation processes, (d) DTPs-ArI-EDB system following the Act-2 activation process and B, B'-2, B6-B10 deactivation processes.

It should be noted that the photo-catalytic cycles presented in Fig. 5 and Fig. S7 are the main efficient mechanisms with low barriers in both activation and deactivation for the propagation of the polymerization process. There are still, however, other possible reactions, even background or side reactions that would occur at the same time, which all need to be considered. Although Ph-$DTP^{\bullet+}$ and $Ar^{\bullet}$ will initiate photopolymerization, this will also result in biradical termination as the background reaction, giving rise to dead chain propagation. The existence of intermediate complexes, such as Ph-$DTP^{\bullet+}$-ArI, Ph-$DTP^{\bullet+}$-I^-, $EDB^{\bullet+}$-ArI and $EDB^{\bullet+}$-I^- will also promote the catalytic cycle, but through different reactions and alternative mechanisms. However, in view of the rather low concentrations of these intermediates, their relevant regeneration processes will be carried out at slow rates, which may be even slower than the biradical termination process, resulting in a loss of the system's photo-catalytic capacity. Additionally, when the catalyst is in the excited state Ph-DTP*, it is a strong reductant, and the generated radical can be reduced to a carbanion state. In accordance with the strong redox potential of Ph-DTP$^{\bullet+}$, there is also a plausible situation whereby the I^- species could be oxidized to I_2, which will generate $I^\bullet$ on irradiation and initiate the propagation of polymerization. However, it must be noted that in practice, the above mentioned background or side reactions will inevitably decrease the reactivity of individual components and overall activity of the PC in the photo-catalytic cycle.

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