Electronic Supplementary Information (ESI) for:

Entropy-Controlled Biradical–Quinoid Isomerization of A π-Conjugated Delocalized Biradical

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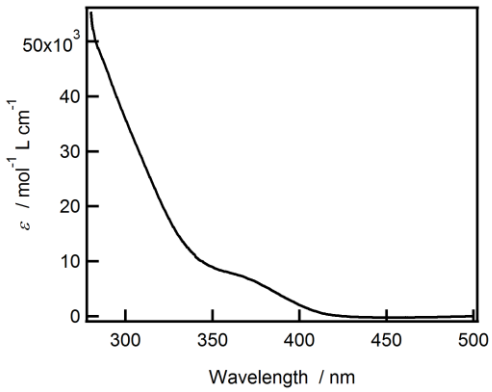

Fig. S1 UV–vis absorption spectrum of tF-BDPI-2YD in benzene.

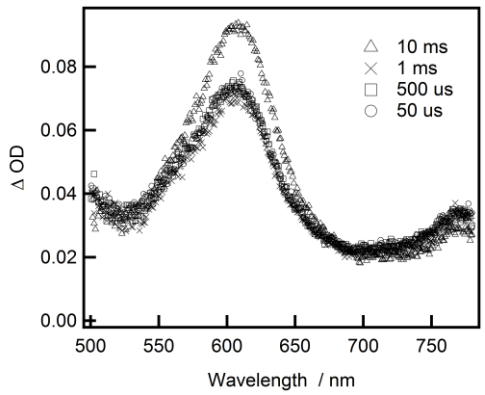

Fig. S2 Transient absorption spectra of tF-BDPI-2YD in benzene at 298 K (7×10^{-5} M; 2 mm light path length). Each spectrum was recorded at 50 μs, 500 μs, 1 ms and 10 ms after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 0.2 mJ/pulse).

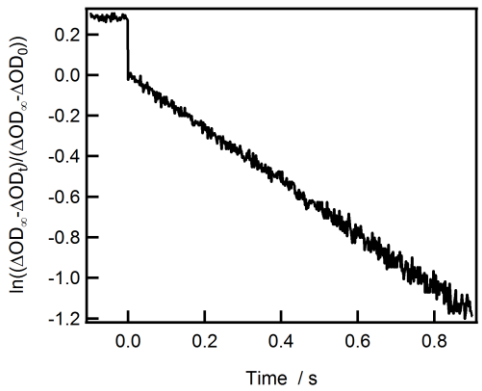

Fig. S3 First-order plots for the transient absorption dynamics of tF-BDPI-2YD at 605 nm in benzene at 298 K.

The effect of O_2 on the biradical–quinoid thermal isomerization

The thermal biradical–quinoid isomerization can be described through the possible two pathways as follows: (i) the intersystem crossing from the photo-generated triplet biradical state to the singlet biradical state has a large activation energy like delayed fluorescence, resulting in the long lifetime of the triplet species and the fast isomerization between singlet biradical and quinoid states. (ii) The singlet biradical species cannot overcome the large activation barrier for the biradical–quinoid isomerization due to the large bond alternation around the central phenylene group. In the case of (i), the singlet and triplet states would be produced in a 1:3 ratio after the C–N bond cleavage because those two states are almost degenerated, suggested by the ESR signal which does not show a clear fine structure (reference 33 in the main text). When singlet and triplet states are degenerated, it is difficult to consider that the intersystem crossing needs high thermal energy. In addition, the absorption band of the quinoid species at 609 nm should be observed even though the weak UV light is irradiated to the tF-BDPI-2YD solution, which is conflicted to the experimental results. Moreover, the thermal isomerization rate does not depend on the concentration of O_2 (Fig. S4) which is the general triplet state quencher. Therefore, we concluded the slow thermal isomerization is due to the activation free energy between the singlet biradical and quinoid species (ii).

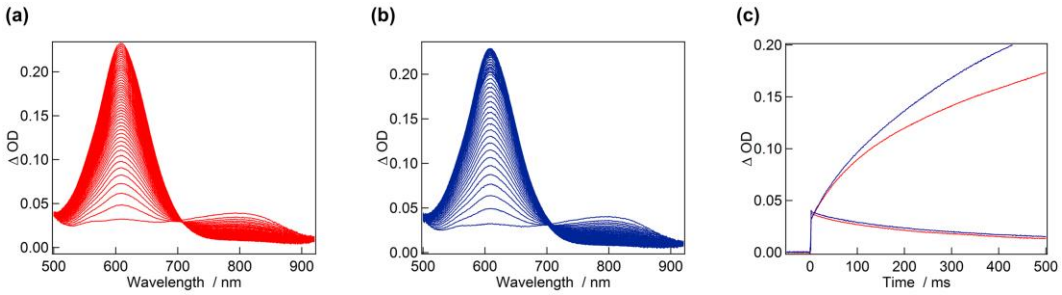

Fig. S4 Transient absorption spectra of tF-BDPI-2YD in benzene under (a) air and (b) O_2 at 298 K (4.5×10^{-5} M; 10 mm light path length). Each of the spectra was recorded at 20 ms intervals from 2 ms after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse). (c) Time profiles of the ΔOD values at 605 and 800 nm, (red) air and (blue) with O_2 bubbling.

The rate constants for the biradical–quinoid thermal isomerization

Table S1 First-order rate constants for the time profiles of the ΔOD at 605 nm of the thermal isomerization reaction from biradical to quinoid species, estimated as the results of the average for at least 9 times measurements.

T / K	k / s^{-1}	standard deviation
278	1.503	0.039
283	1.472	0.098
288	1.443	0.080
293	1.414	0.092
298	1.391	0.073
303	1.358	0.072
308	1.333	0.101
313	1.329	0.073