Supporting Information

1. Synthesis of compounds

All reagents and solvents were of the commercial reagent grade and were used without further purification except dimethylformamide, which was obtained by refluxing and distilling. 1H-NMR spectra were recorded on a JEOL ALPHA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (= 7.260). Mass spectra were recorded on a JEOL HX-110 spectrometer, using positive-FAB ionization method with accelerating voltage 10 kV and a 3-nitrobenzylalcohol matrix. Preparative separations were performed by silica gel flash column chromatography (Merck Kieselgel 60H Art. 7736) and silica gel gravity column chromatography (Wako gel C-200). Recycling GPC-HPLC was carried out on JAI LC-908 using a preparative JAI-GEL-1H column (chloroform eluant; flow rate 3.8 mL min^{-1}).

1,2-Bis(anthracen-9-yl)benzene (*o*-DAB). A solution of 9-anthrylboronic acid (20 mg, 90 mmol), 1,2-diiodobenzene (11 mg, 33 mmol), tetrakis(triphenylphosphino)palladium(0) (7.0 mg, 6 mmol), and Cs_2CO_3 (32 mg 98 mmol) in dry dimethylformamide (3 mL) was degassed three times by freeze-pump-threw and then heated at 90 ºC under argon for 5 h. The solvent was removed by a vacuum distillation. The residue was dissolved in benzene, washed with water and brine, and was dried over anhydrous Na_2SO_4. The solvent was removed and the reaction mixture was separated by a recycling-preparative GPC-HPLC with $CHCl_3$. The product was reprecipitated from $CHCl_3$-MeOH. Yield; 0.6 mg, 4%. 1H NMR ($CDCl_3$) 7.92 (s, 2 H, 10,10'), 7.82 (d, *J* = 10 Hz, 4 H, 1, 1', 8, 8'), 7.79 (s, 4 H, Ph), 7.59 (d, *J* = 9 Hz, 4 H, 4, 4', 5, 5'), 7.13 (t, *J* = 8 Hz, 4 H, 3, 3', 6, 6'), and 6.98 (dt, *J* = 2 Hz, 8 Hz, 4 H, 2, 2', 7, 7'); FAB MS *m/z* 430.14, Calcd for C34H22 *m/z* 430.17; UV-vis (CHCl3) *max* 353, 371, and 393 nm; Fluorescence ($CHCl_3$, *ex* = 350 nm) *em* 398, 420, 444, and 499 (br) nm.

3,5-Bis(anthracen-2-yl)-*t*-butylbenzene (*m*-DAB). A solution of 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-anthracene (50 mg 164 mmol), 3,5-dibromo-*t*-butylbenzene1 (25 mg 84 mmol), $Pd(PPh_3)4$ (16 mg 14 mmol) Cs_2CO_3 (80 mg 250 mmol) in dry dimethylformamide (5 mL) was degassed three times by freeze-pump-threw and then heated at 90 ºC under argon for 4 h. After the usual work-up, recrystallization from $CHCl_3$-MeOH gave the desired product (28%). 1H NMR ($CDCl_3$) 8.54 (s, 2 H, 10, 10'), 8.48 (s, 2 H, 9, 9'), 8.31 (s, 2 H, 1, 1'), 8.13 (d, J = 9 Hz, 2 H, 4, 4'), 8.03 (m, 4 H), 7.98 (t, J = 2 Hz, 1 H, Ph), 7.87 (dd, J = 9 Hz, 2 Hz, 2 H, 3, 3'), 7.83 (d, J = 2 Hz, 2 H, Ph), 7.48 (m, 4 H), and 1.53 (9 H, *t*-Bu); FAB MS *m/z* 486.35, Calcd for $C_{34}H_{22}$ *m/z* 486.23; UV-vis ($CHCl_3$) *max* 335, 351, 369, and 388 nm; Fluorescence ($CHCl_3$, *ex* = 350 nm) *em* 397, 420, and 446 nm.

2. The phase shift δ in the oscillatory curve (Eq 1) and its treatment in the present study

Derivation of of eq 1. Eq 1 is a solution of the differential equation named the optical Bloch equation for the density matrix elements of the respective locally excitated states ρ_{11} and ρ_{22} actually $\Delta n = \rho_{11} - \rho_{22}$ (see Ref. 8):

$$\Delta\ddot{n} + \left(\frac{1}{T_1} + \frac{2}{T_2}\right)\Delta\dot{n} + \left(4\beta^2 + \frac{2}{T_1 T_2}\right)\Delta n = 0 \qquad \text{(S1)}$$

where β is the interaction energy, T_1 is the population decay constant, and T_2 is the phenomenological dephasing time. This equation can be rewritten by using a relation $1/T_2 = 1/(2T_1) + 1/T_2'$ where T_2' is the pure dephasing time (i.e., the decay of ρ_{12}) as:

$$\Delta\ddot{n} + 2\left(\frac{1}{T_1} + \frac{1}{T_2'}\right)\Delta\dot{n} + \left(4\beta^2 + \frac{1}{T_1^2} + \frac{2}{T_1 T_2'}\right)\Delta n = 0 \qquad \text{(S2)}$$

The differential equation (eq S2) can be solved for the cases depending on the relative magnitudes of the interaction energy 2β and the energy width of dephasing process (T_2'). In the underdamped condition $2\beta T_2' > 1$, a general solution is obtained as follows:

$$\Delta n(t) = e^{-\mu t}\left[A\, e^{i\omega_{\mathrm{osc}} t} + A^{*} e^{-i\omega_{\mathrm{osc}} t}\right] \qquad \text{(S3)}$$

where $\omega_{\mathrm{osc}} = \sqrt{4\beta^2 - \left(\frac{1}{T_2'}\right)^2}$, $\mu = \frac{1}{T_1} + \frac{1}{T_2'}$, A and A* (complex conjugate of A) are constants which are determined from the initial conditions. Eq S3 can be rewritten by using the well-known relations between sine, cosine and the exponential function as follows:

$$\Delta n(t) = e^{-\mu t}\left[(A + A^{*})\cos(\omega_{\mathrm{osc}} t) + i(A - A^{*})\sin(\omega_{\mathrm{osc}} t)\right] \qquad \text{(S4)}$$

Substituting into eq S4 the initial conditions at $t = 0$, i.e., $\Delta n(0) = \Delta n_0$ and $(\mathrm{d}\Delta n / \mathrm{d}t)_{t=0} = -(\Delta n_0 / T_1)$, we obtain

$$\Delta n(t) = \Delta n_0\, e^{-\mu t}\left[\cos(\omega_{\mathrm{osc}} t) + \frac{1}{\omega_{\mathrm{osc}} T_2'}\sin(\omega_{\mathrm{osc}} t)\right] \qquad \text{(S5)}$$

We obtain an equivalent expression for $\Delta n(t)$ using a cosine under the same initial conditions as before:

$$\Delta n(t) = \frac{\Delta n_0}{\cos\delta}\, e^{-\mu t}\cos(\omega_{\mathrm{osc}} t + \delta) \qquad \text{(S6)}$$

where δ is the initial phase which is related to ω_{ocs} and T_2' as $\tan\delta = -(\omega_{\mathrm{ocs}} T_2')^{-1}$. Thus we obtain eq 1 in the text.

On the phase shift δ in this study. In the present analyses, δ is treated as a varying parameter to obtain a theoretical curve best fitted to the experimental one on the whole time range. The δ value is, however, the initial phase of the oscillation which depends directly on the initial quantum state just after the laser pulse excitation. As shown in Figure 3, the observed $r(t)$ curves do not fit the theoretical curve in the initial time region <0.3 ps, particularly in *o*-DAB. Presumably an ultrafast relaxation path may be involved in the relaxation process, other than the dominant coherent process. In this respect, we do not discuss anymore on the phase shift in the present paper. We are now proceeding to more detailed analysis for this problem on the basis of more accurate reaction scheme.