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Electronic Supporting Information for

Synthetic control over intra- and intermolecular charge transfer can turn on fluorescence emission of non-emissive coumarin

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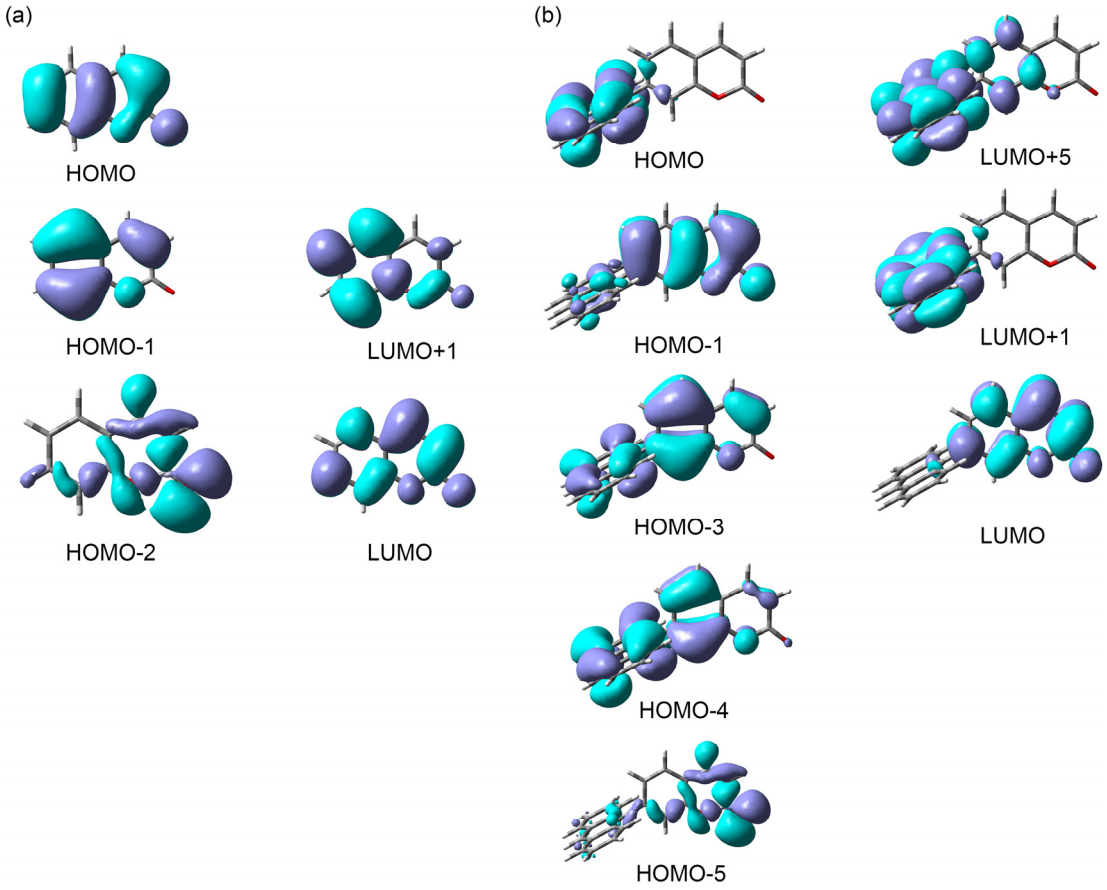

Fig. S1. Isodensity surface plots of the molecular orbitals of (a) C and (b) AC.

Table S1. Summary of the TD–DFT Calculation Results for the Coumarin Compounds

1) C

state	energy (eV)	oscillator strength	participating molecular orbitals (expansion coefficient)
T_1	2.847	0	HOMO → LUMO (0.62)
T_2	3.530	0	HOMO−1 → LUMO (0.59)
T_3	4.077	0	HOMO → LUMO+1 (0.46)
S_1	4.108	0.1839	HOMO → LUMO (0.65)
T_4	4.439	0	HOMO−2 → LUMO (0.67)
S_2	4.458	0.2399	HOMO−1 → LUMO (0.63)
T_5	4.592	0	HOMO → LUMO+2 (0.46)
T_6	4.745	0	HOMO−1 → LUMO+1 (0.62)
S_3	4.782	0	HOMO−2 → LUMO (0.69)

T_7	5.131	0	HOMO → LUMO+2 (0.62)
S_4	5.403	0.0123	HOMO → LUMO+1 (0.46)
T_8	5.516	0	HOMO−1 → LUMO+1 (0.58)
S_5	5.724	0.1641	HOMO → LUMO+1 (0.50)
T_9	6.006	0	HOMO−5 → LUMO (0.55)
S_6	6.034	0.4219	HOMO−1 → LUMO+1 (0.49)
T_{10}	6.035	0	HOMO−4 → LUMO (0.58)
T_{11}	6.153	0	HOMO → LUMO+3 (0.68)
S_7	6.182	0.0059	HOMO → LUMO+3 (0.69)
S_8	6.221	0.3498	HOMO−1 → LUMO+2 (0.60)
S_9	6.289	0.0001	HOMO−4 → LUMO (0.59)

2) PC

state	energy (eV)	oscillator strength	participating molecular orbitals (expansion coefficient)
T_1	2.665	0	HOMO → LUMO (0.65)
T_2	3.431	0	HOMO−1 → LUMO (0.59)
T_3	3.631	0	HOMO−3 → LUMO (0.43)
S_1	3.767	0.6924	HOMO → LUMO (0.70)
T_4	4.028	0	HOMO−1 → LUMO+2 (0.65)
T_5	4.137	0	HOMO−2 → LUMO (0.62)
S_2	4.154	0.0225	HOMO−1 → LUMO (0.67)
T_6	4.260	0	HOMO−2 → LUMO+2 (0.65)
T_7	4.418	0	HOMO−4 → LUMO (0.65)
S_3	4.429	0.0067	HOMO−2 → LUMO (0.68)
T_8	4.504	0	HOMO → LUMO+2 (0.40)
T_9	4.582	0	HOMO → LUMO+2 (0.40)
T_{10}	4.614	0	HOMO → LUMO+3 (0.58)
T_{11}	4.707	0	HOMO−2 → LUMO+3 (0.33)
S_4	4.735	0.0146	HOMO−4 → LUMO (0.59)
S_5	4.808	0.0440	HOMO−3 → LUMO (0.54)
T_{12}	4.995	0	HOMO−1 → LUMO+1 (0.55)
S_6	5.044	0.1197	HOMO → LUMO+1 (0.57)
S_7	5.064	0.0570	HOMO → LUMO+2 (0.49)
S_8	5.155	0.0258	HOMO → LUMO+3 (0.56)

3) NC

state	energy (eV)	oscillator strength	participating molecular orbitals (expansion coefficient)
T_1	2.589	0	HOMO → LUMO (0.48)
T_2	2.815	0	HOMO−1 → LUMO (0.46)
S_1	3.393	0.3027	HOMO → LUMO (0.70)
T_3	3.513	0	HOMO−3 → LUMO (0.59)
T_4	3.558	0	HOMO → LUMO (0.48)
T_5	3.850	0	HOMO−2 → LUMO+1 (0.37)
T_6	3.987	0	HOMO−1 → LUMO+2 (0.26)
S_2	4.064	0.2058	HOMO−1 → LUMO (0.62)
T_7	4.084	0	HOMO → LUMO+2 (0.44)
S_3	4.168	0.0688	HOMO → LUMO+1 (0.52)
T_8	4.172	0	HOMO−4 → LUMO+1 (0.32)
S_4	4.239	0.0098	HOMO−2 → LUMO (0.46)
T_9	4.362	0	HOMO−2 → LUMO+2 (0.43)
S_5	4.365	0.2008	HOMO−3 → LUMO (0.59)
T_{10}	4.418	0	HOMO−6 → LUMO (0.25)
T_{11}	4.428	0	HOMO−5 → LUMO (0.58)
T_{12}	4.477	0	HOMO−2 → LUMO+1 (0.44)
S_6	4.495	0.0259	HOMO → LUMO+2 (0.40)
T_{13}	4.547	0	HOMO−3 → LUMO+2 (0.35)
S_7	4.744	0.0167	HOMO → LUMO+3 (0.49)

4) AC

state	energy (eV)	oscillator strength	participating molecular orbitals (expansion coefficient)
T_1	1.802	0	HOMO → LUMO+1 (0.70)
T_2	2.815	0	HOMO−1 → LUMO (0.45)
T_3	2.930	0	HOMO → LUMO (0.70)
S_1	2.937	0.0003	HOMO → LUMO (0.70)
S_2	3.111	0.1608	HOMO → LUMO+1 (0.70)
T_4	3.289	0	HOMO−4 → LUMO+1 (0.39)
T_5	3.459	0	HOMO−2 → LUMO+1 (0.50)
T_6	3.523	0	HOMO−3 → LUMO (0.51)
T_7	3.523	0	HOMO−3 → LUMO (0.51)

T_8	3.625	0	HOMO → LUMO+2 (0.47)
S_3	3.796	0.0004	HOMO−4 → LUMO (0.20)
T_9	4.042	0	HOMO−1 → LUMO+2 (0.32)
S_4	4.061	0.2480	HOMO−1 → LUMO (0.65)
T_{10}	4.095	0	HOMO−6 → LUMO+1 (0.41)
T_{11}	4.096	0	HOMO−1 → LUMO+1 (0.66)
S_5	4.100	0.0027	HOMO−1 → LUMO+1 (0.68)
S_6	4.217	0.0304	HOMO → LUMO+3 (0.53)
T_{12}	4.227	0	HOMO → LUMO+3 (0.54)
T_{13}	4.229	0	HOMO−2 → LUMO (0.66)
S_7	4.240	0.0413	HOMO−2 → LUMO (0.71)

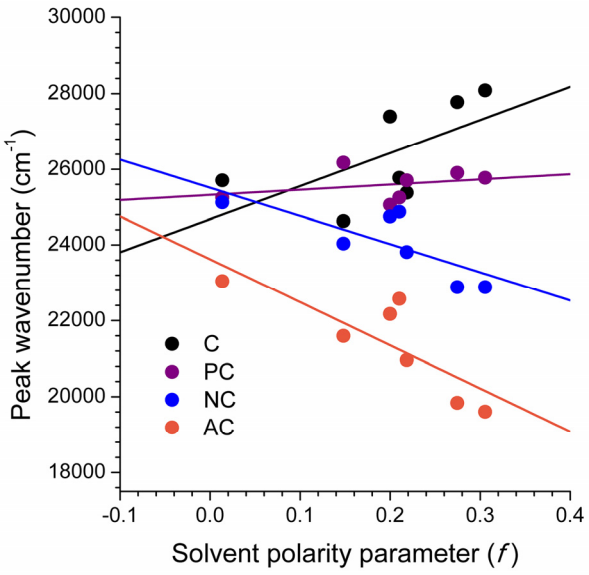

Fig. S2. Lippert–Mataga plot for the fluorescence emission of the coumarin compounds.

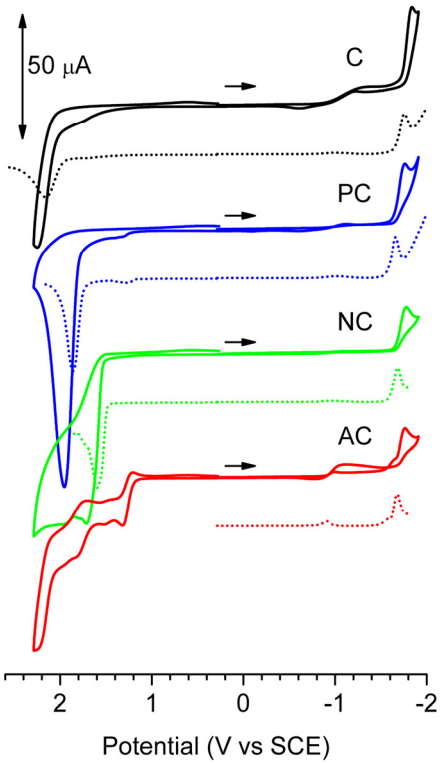

Fig. S3. Cyclic (solid curves) and differential pulse (dotted curves) voltammograms of the coumarin compounds. Conditions: A Pt wire and a Pt disc as the counter and working electrodes, respectively; $Ag/AgNO_3$ as a pseudo reference electrode; 2.0 mM solutions in Ar-saturated CH_3CN containing 0.10 M $TBAPF_6$ electrolyte; scan rates = 100 mV s^{-1} and 4 mV s^{-1} for cyclic and differential pulse voltammetry, respectively.

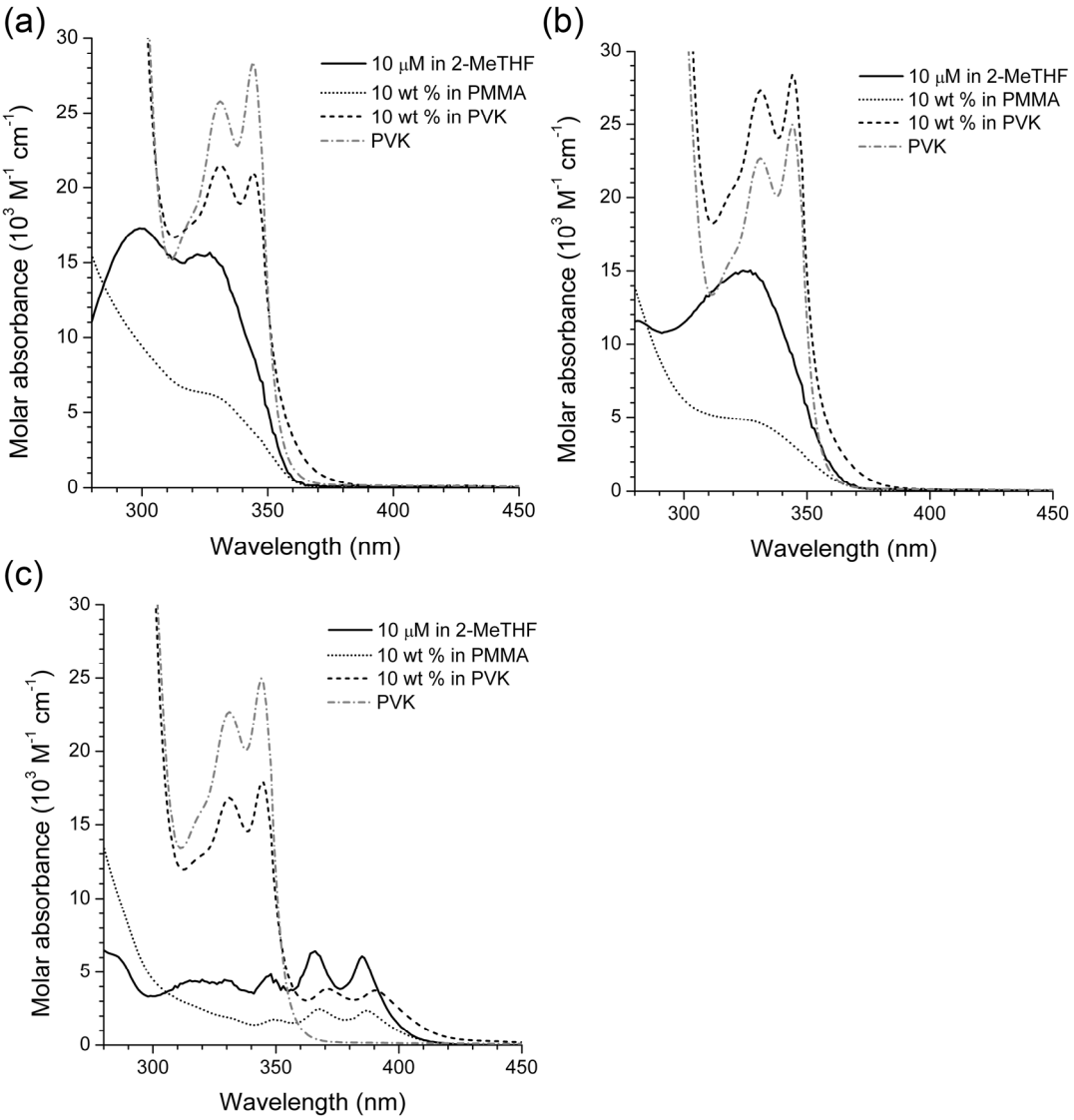

Fig. S4. UV–vis absorption spectra of the coumarin compounds measured in fluid (10 μM in 2-MeTHF) and solid (10 wt % in PMMA or PVK) solutions. Absorption spectra of PVK are included for comparison: (a) PC, (b) NC, and (c) AC.

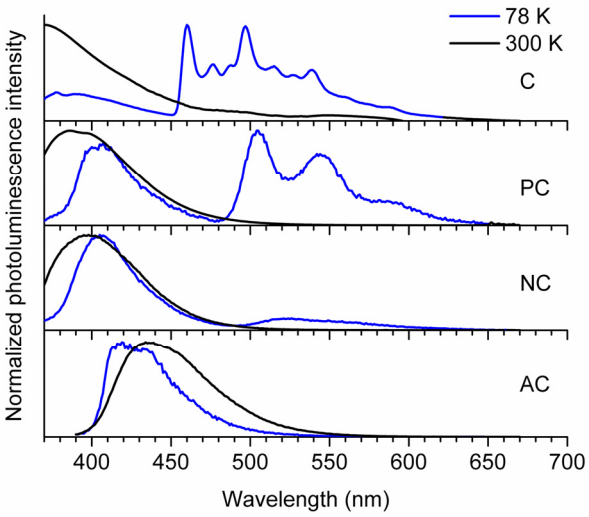

Fig. S5. Photoluminescence spectra of 50 μM coumarin compounds in 2-MeTHF (C) and iodoethane (PC, NC and AC) obtained at 78 K (blue curves) and 300 K (black curves).

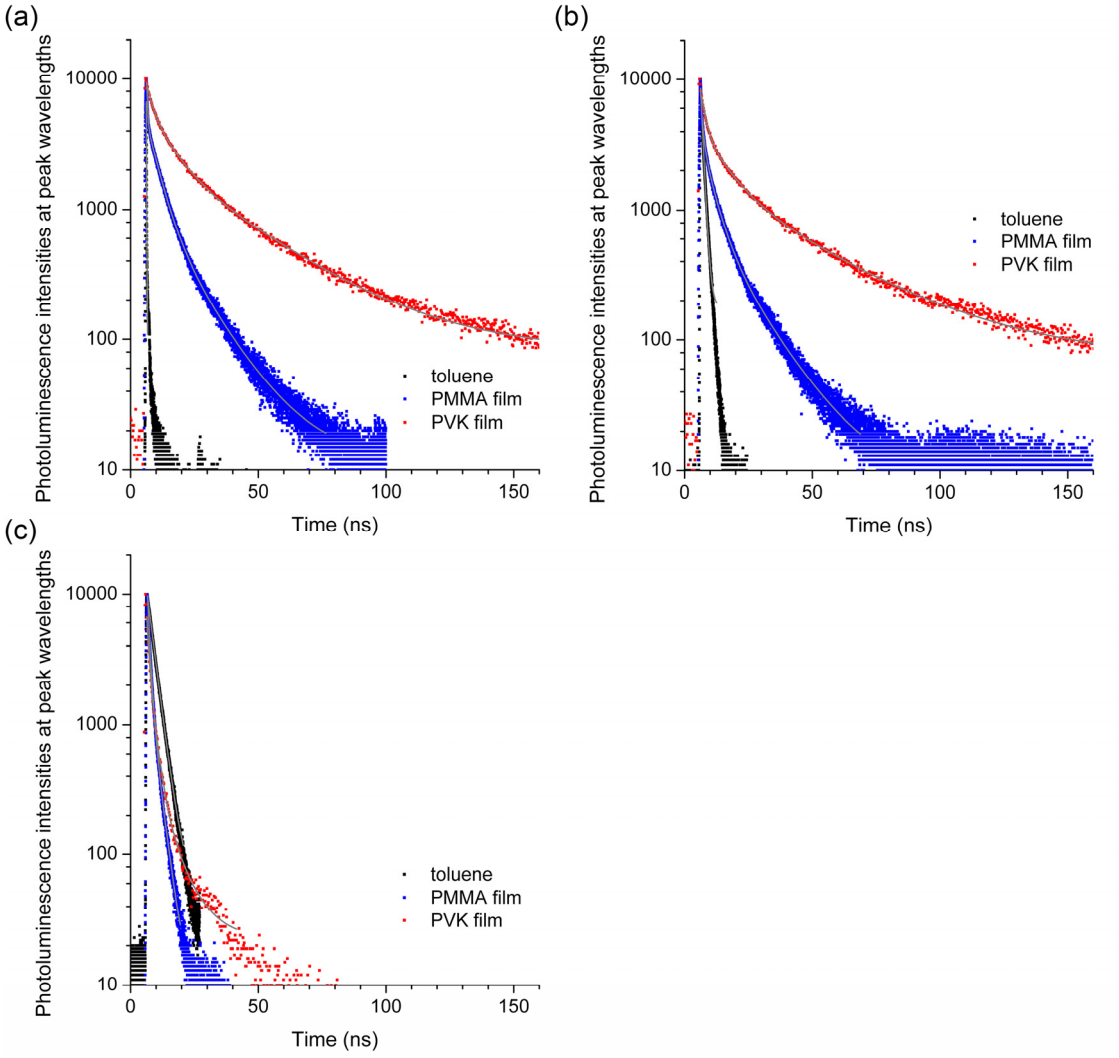

Fig. S6. Photoluminescence decay traces of (a) C, (b) PC, and (c) AC after ps pulsed laser excitation at 377 nm (pulse duration = 8 ps): black, 50 μM in Ar-saturated toluene; blue, 10 wt % in PMMA film; red, 10 wt % in PVK film. Grey curves are non-linear least squares fits to monoexponential (black) and biexponential (blue and red) decay models. Refer to Table 1 for the fit results.

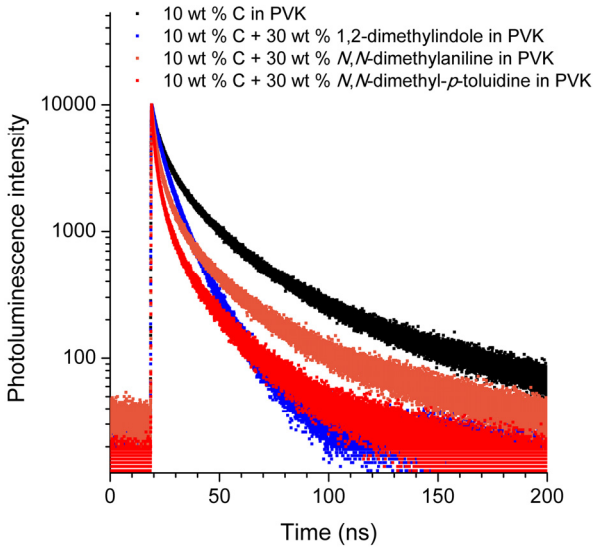

Fig. S7. Photoluminescence decay traces of PVK films containing 10 wt % C and 30 wt % electron donors after picosecond pulsed laser excitation at 377 nm.

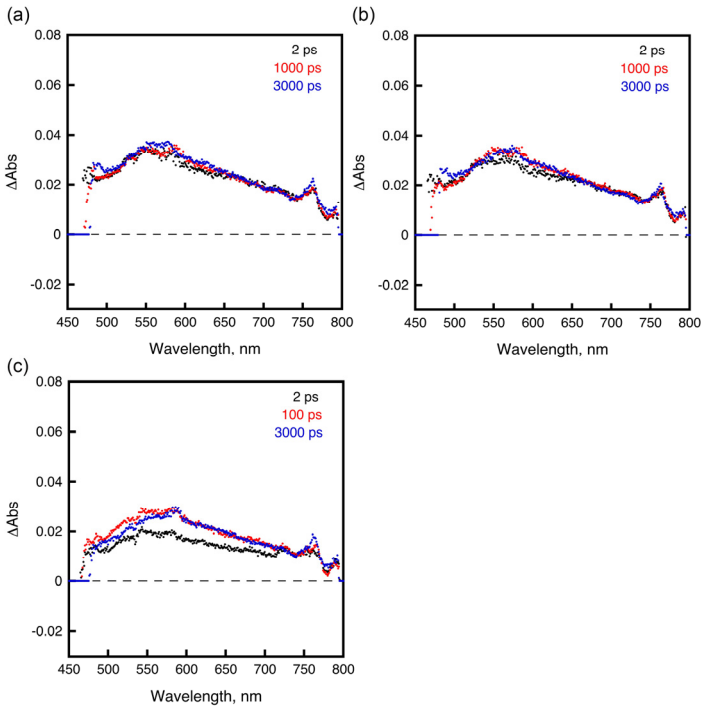

Fig. S8. Transient absorption spectra of toluene solutions containing (a) C, (b) PC, (c) NC, and (d) AC recorded at 2, 100, and 3000 ps delay after femtosecond pulse laser excitation at 330 nm (C) and 350 nm (PC, NC, and AC).

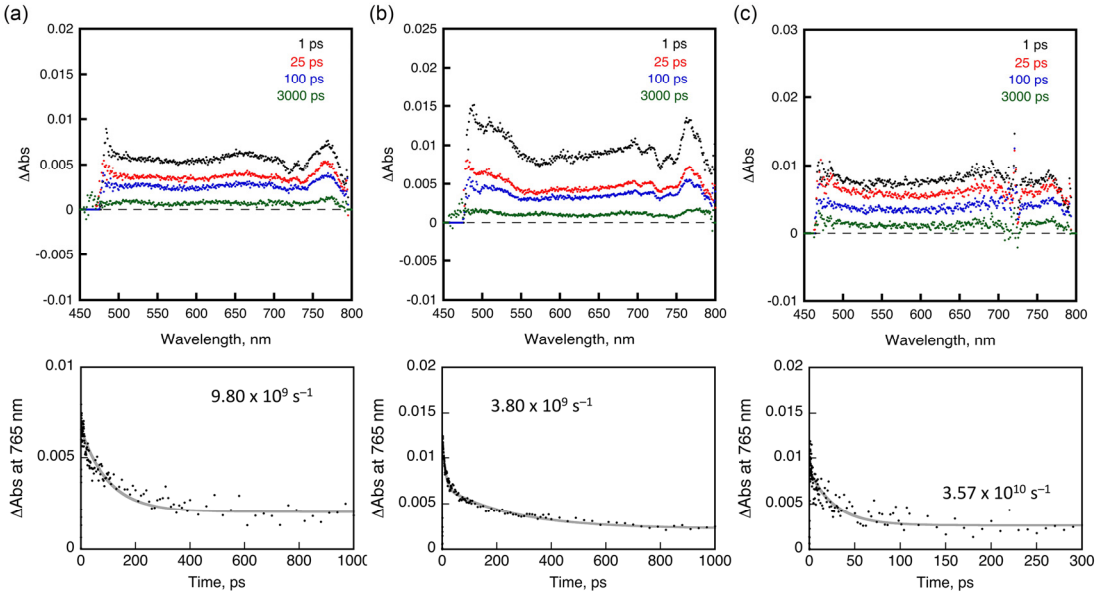

Fig. S9. Femtosecond laser flash photolysis of PVK films doped with (a) 10 wt % C, (b) 10 wt % NC, and (c) 10 wt % AC: Top, transient absorption spectra recorded at 1, 25, 100, and 1000 ps after photoexcitation at 330 nm; bottom, decay traces of the transient absorption at 765 nm and non-linear least squares fits to a biexponential decay model.

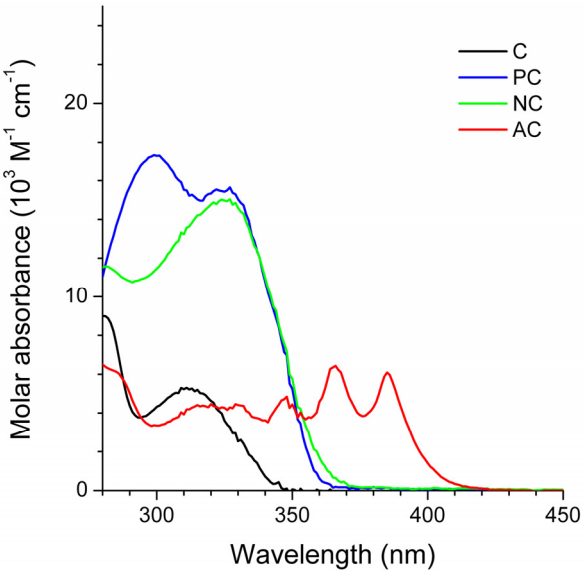

Fig. S10. UV–vis absorption spectra of the coumarin compounds in 2-MeTHF.

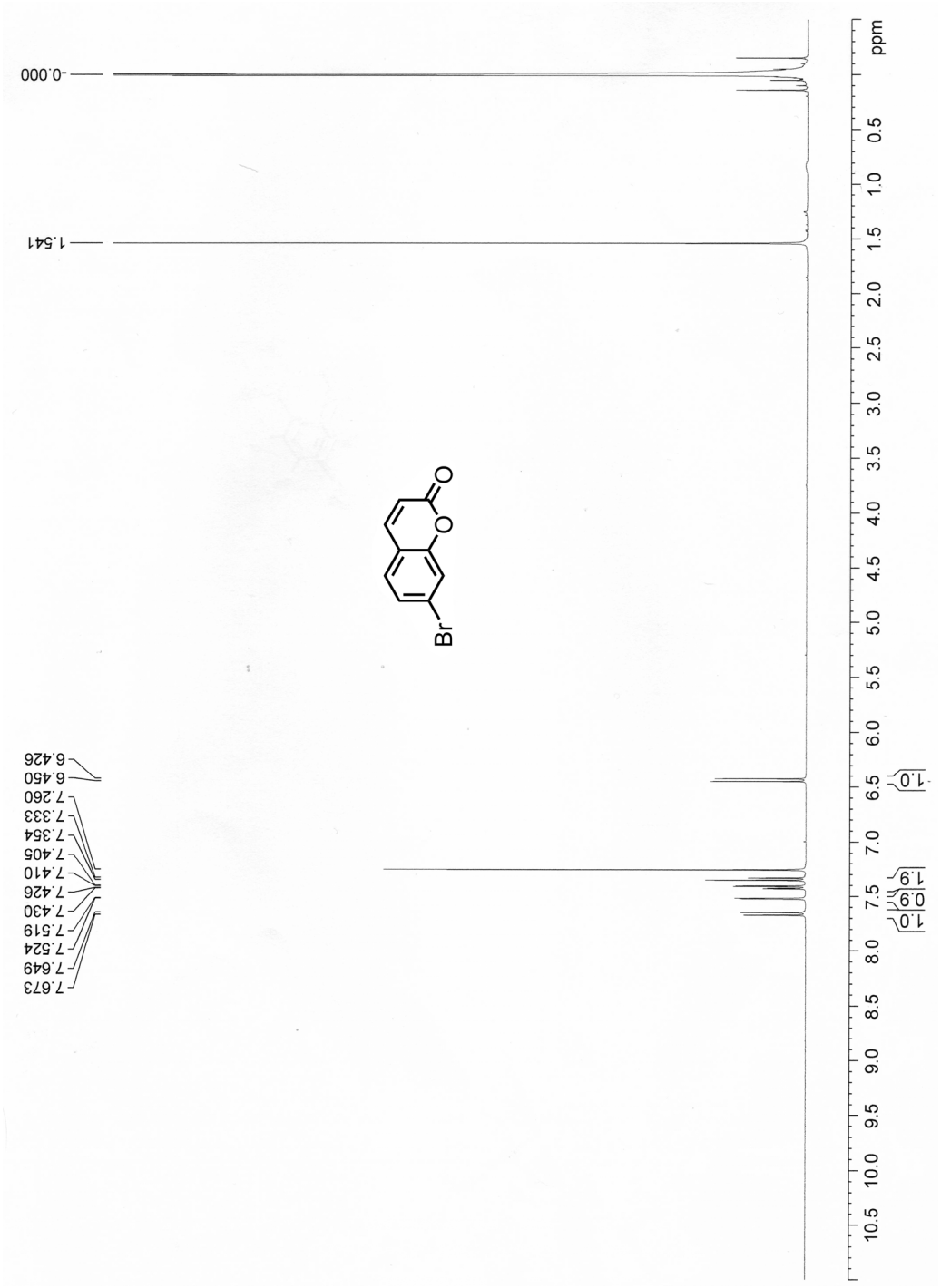

Fig. S11. ^{1}H NMR spectrum of 9-bromocoumarin ($CDCl_3$, 400 MHz).

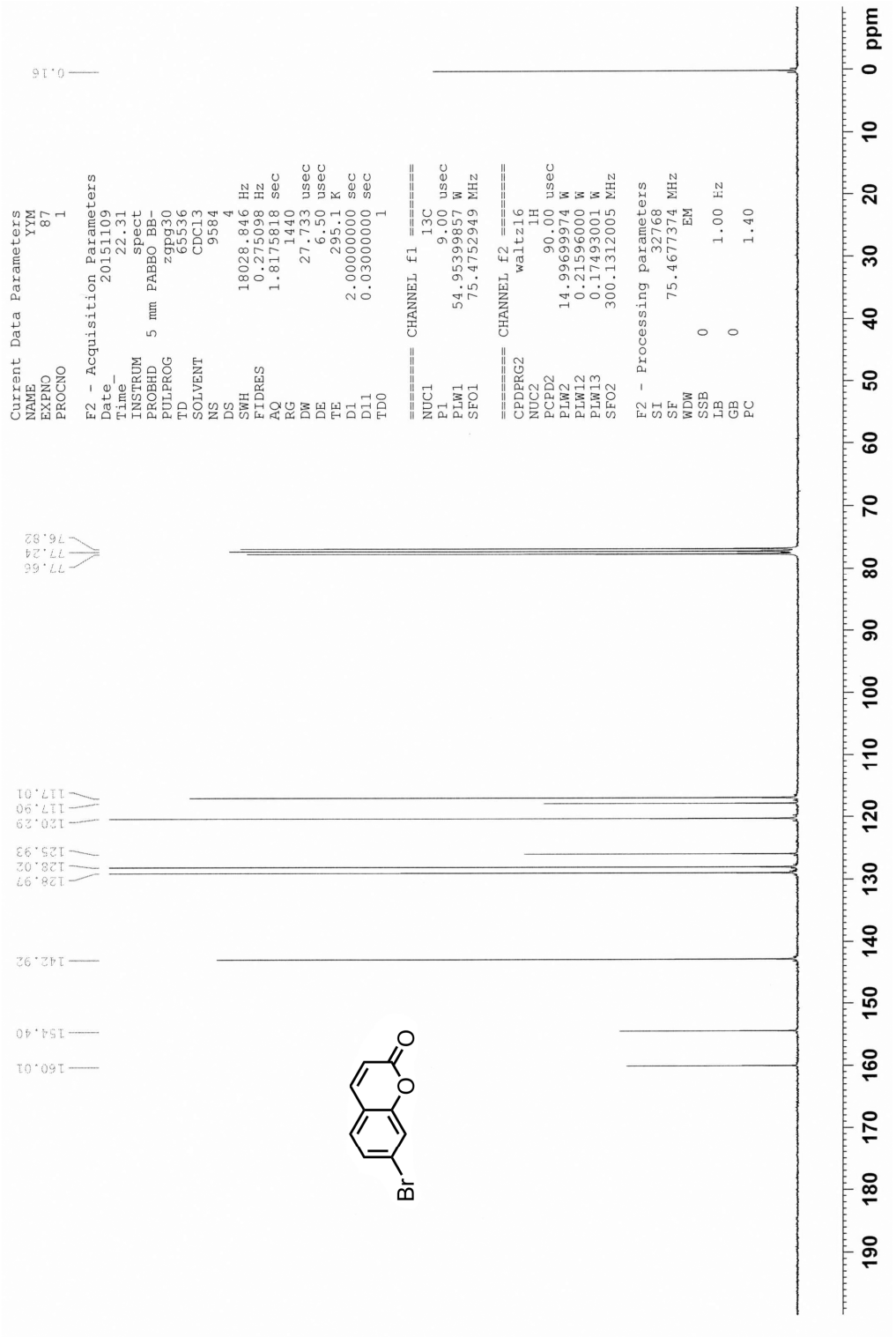

Fig. S12. $^{13}C\{^{1}H\}$ NMR spectrum of 9-bromocoumarin ($CDCl_3$, 75 MHz).

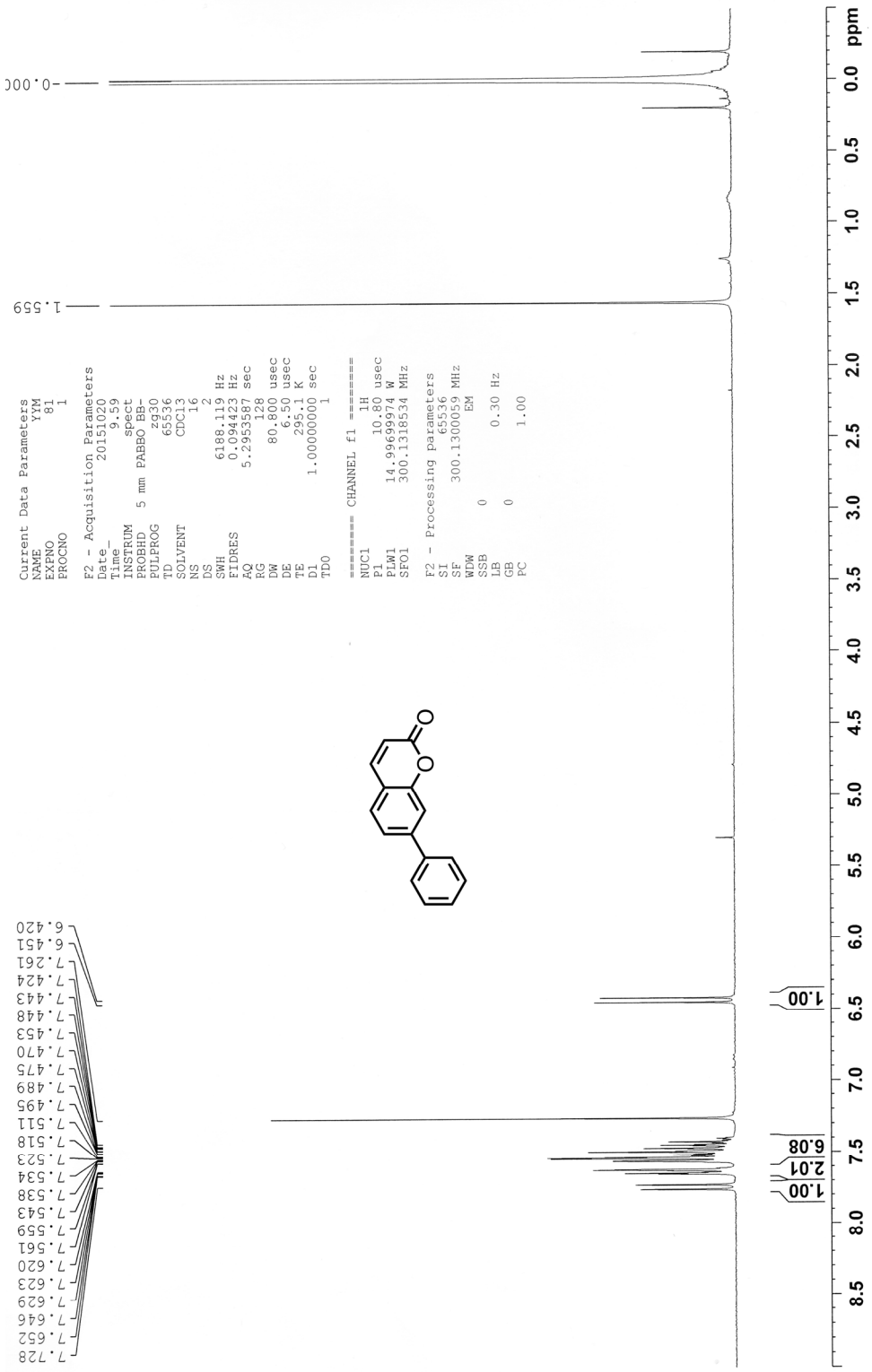

Fig. S13. ^{1}H NMR spectrum of PC ($CDCl_3$, 300 MHz).

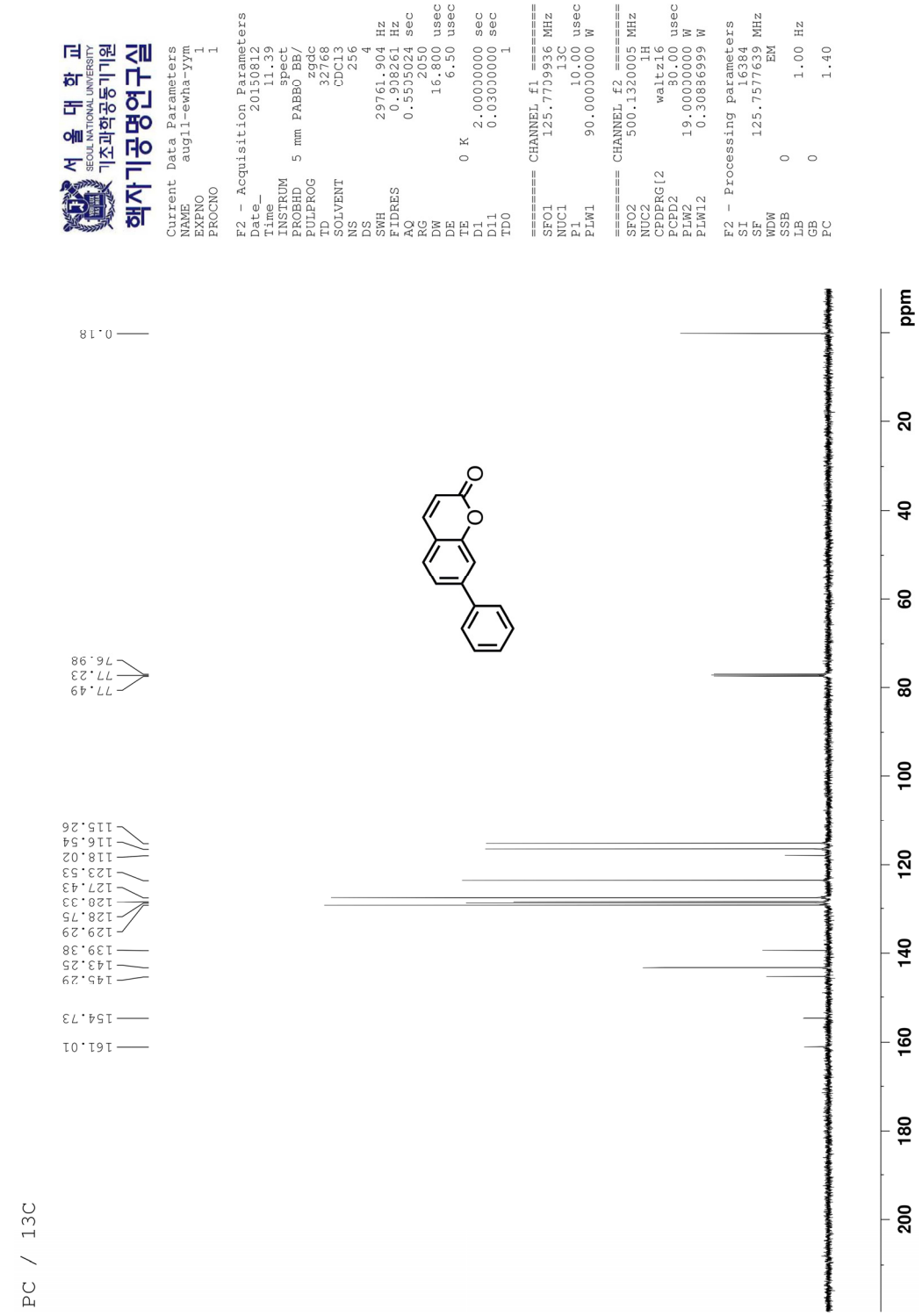

Fig. S14. $^{13}C\{^{1}H\}$ NMR spectrum of PC ($CDCl_3$, 126 MHz).

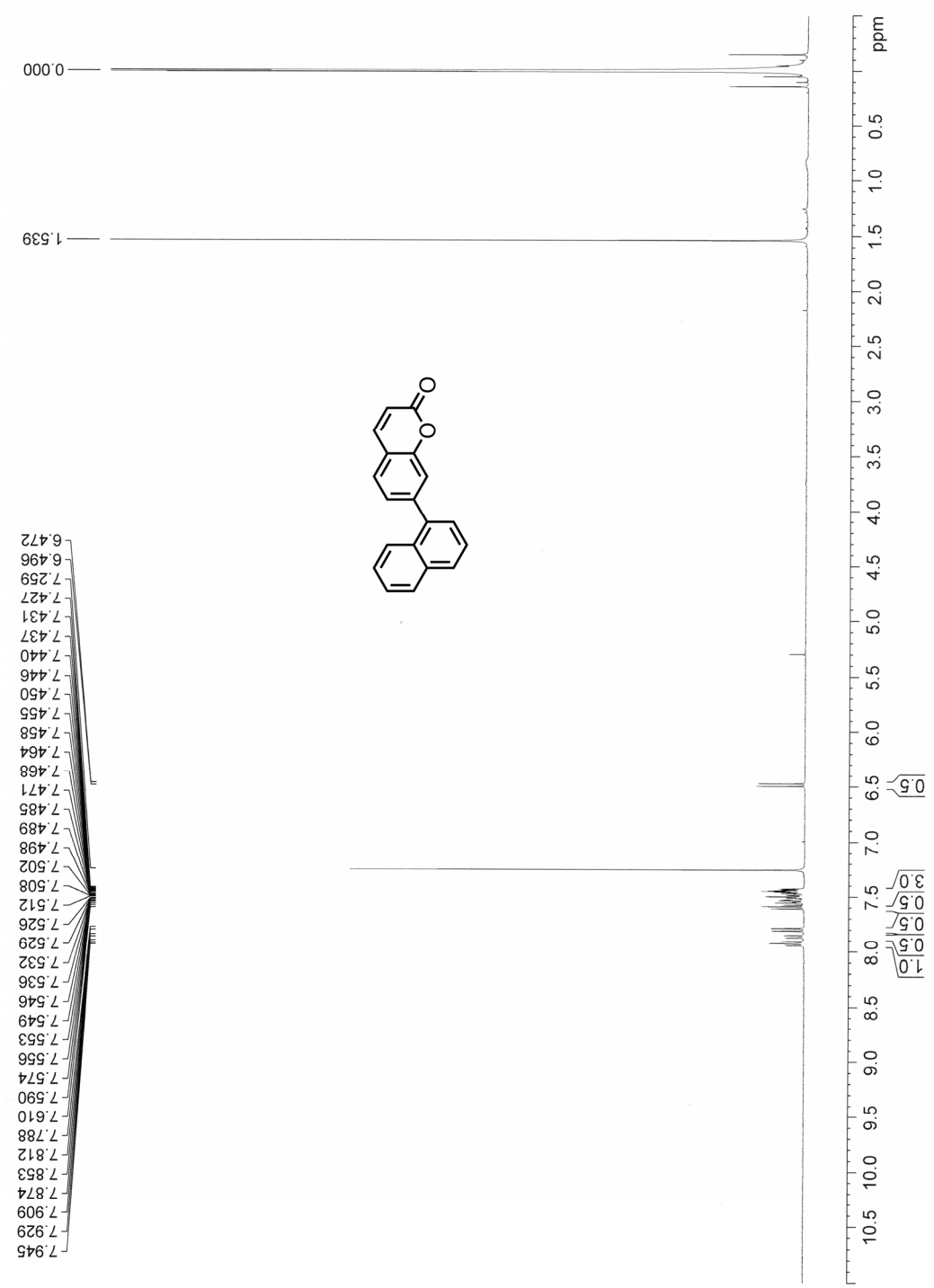

Fig. S15. ^{1}H NMR spectrum of NC ($CDCl_3$, 300 MHz).

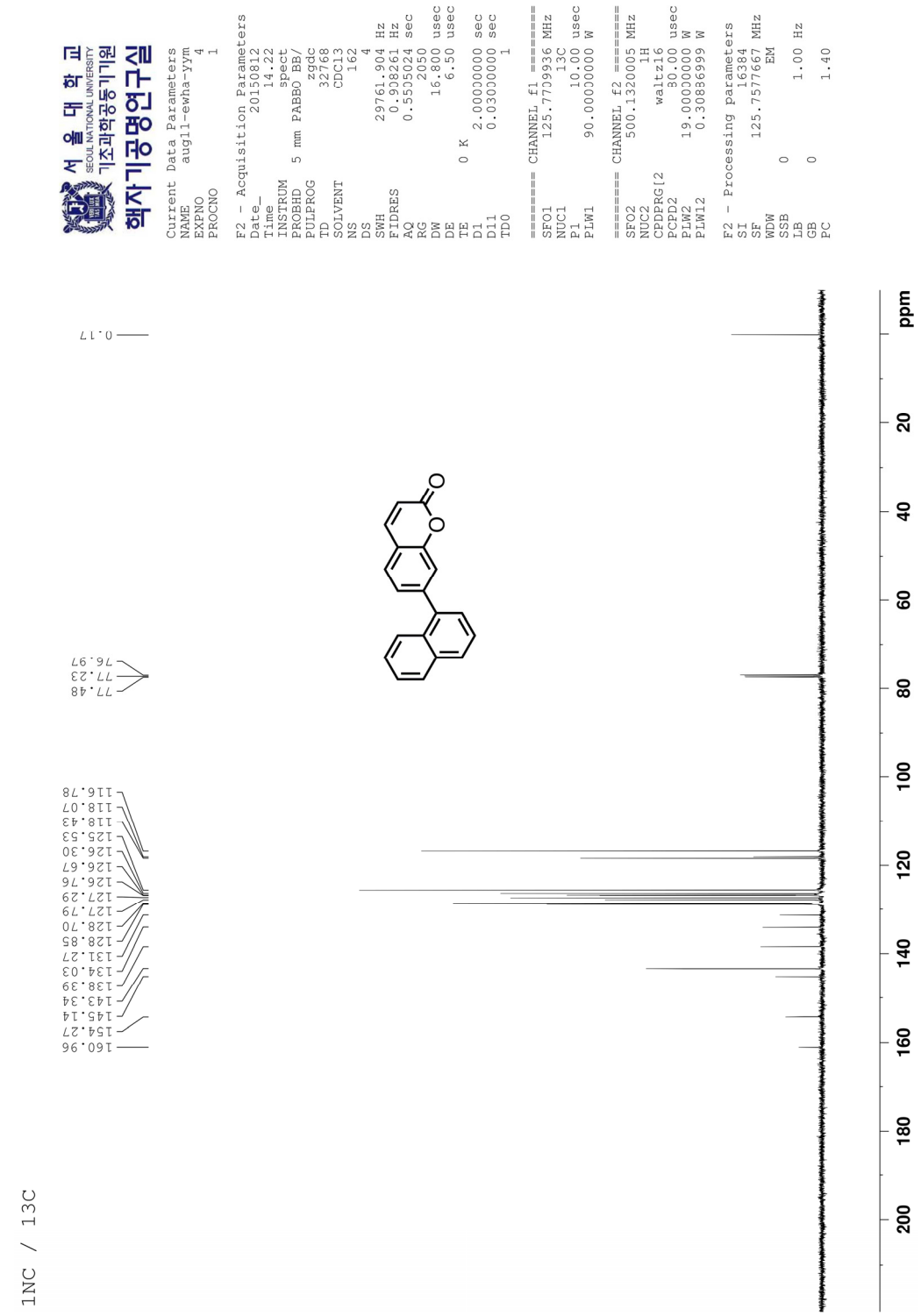

Fig. S16. $^{13}C\{^{1}H\}$ NMR spectrum of NC ($CDCl_3$, 126 MHz).

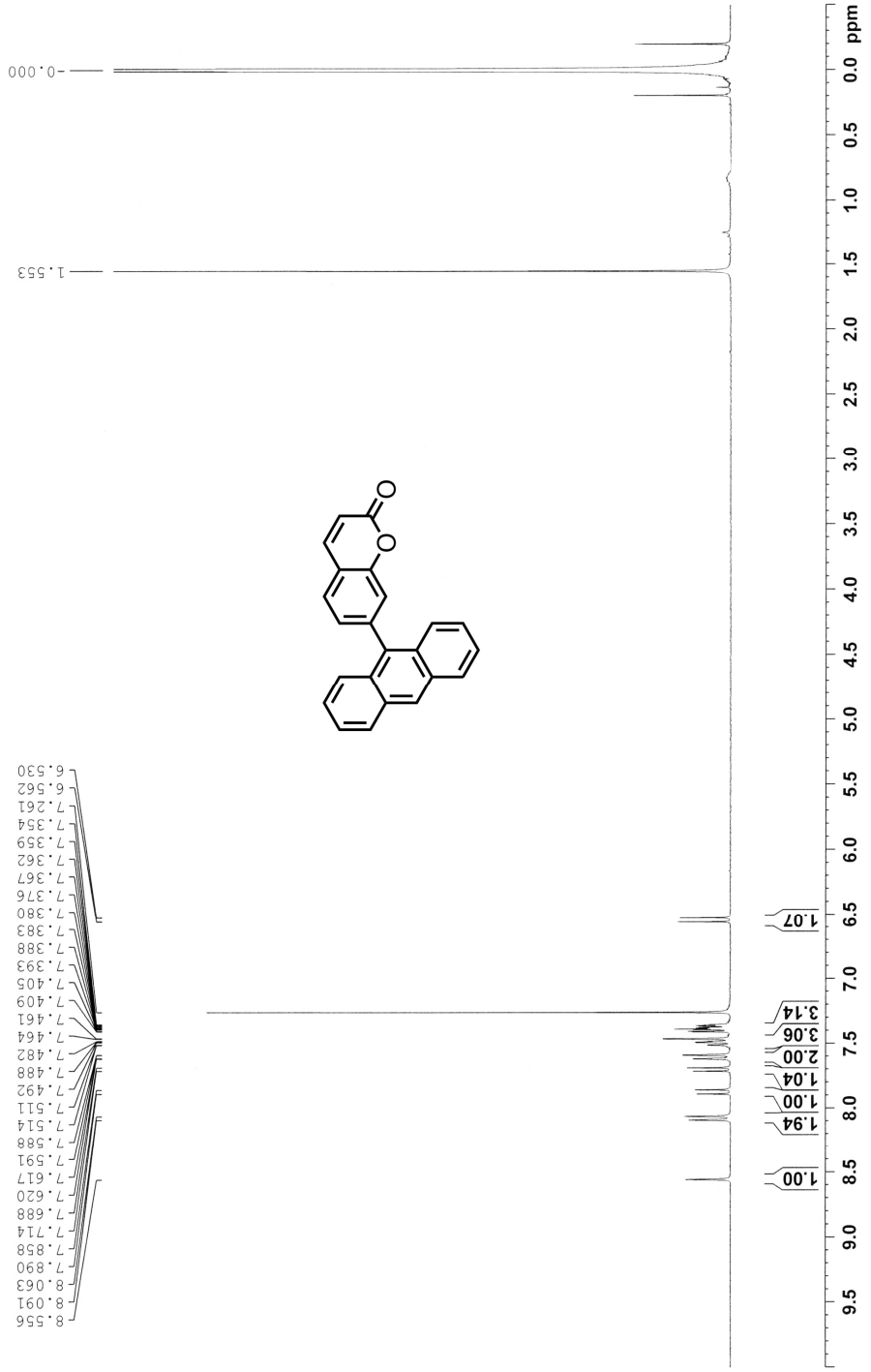

Fig. S17. ^{1}H NMR spectrum of AC ($CDCl_3$, 300 MHz).

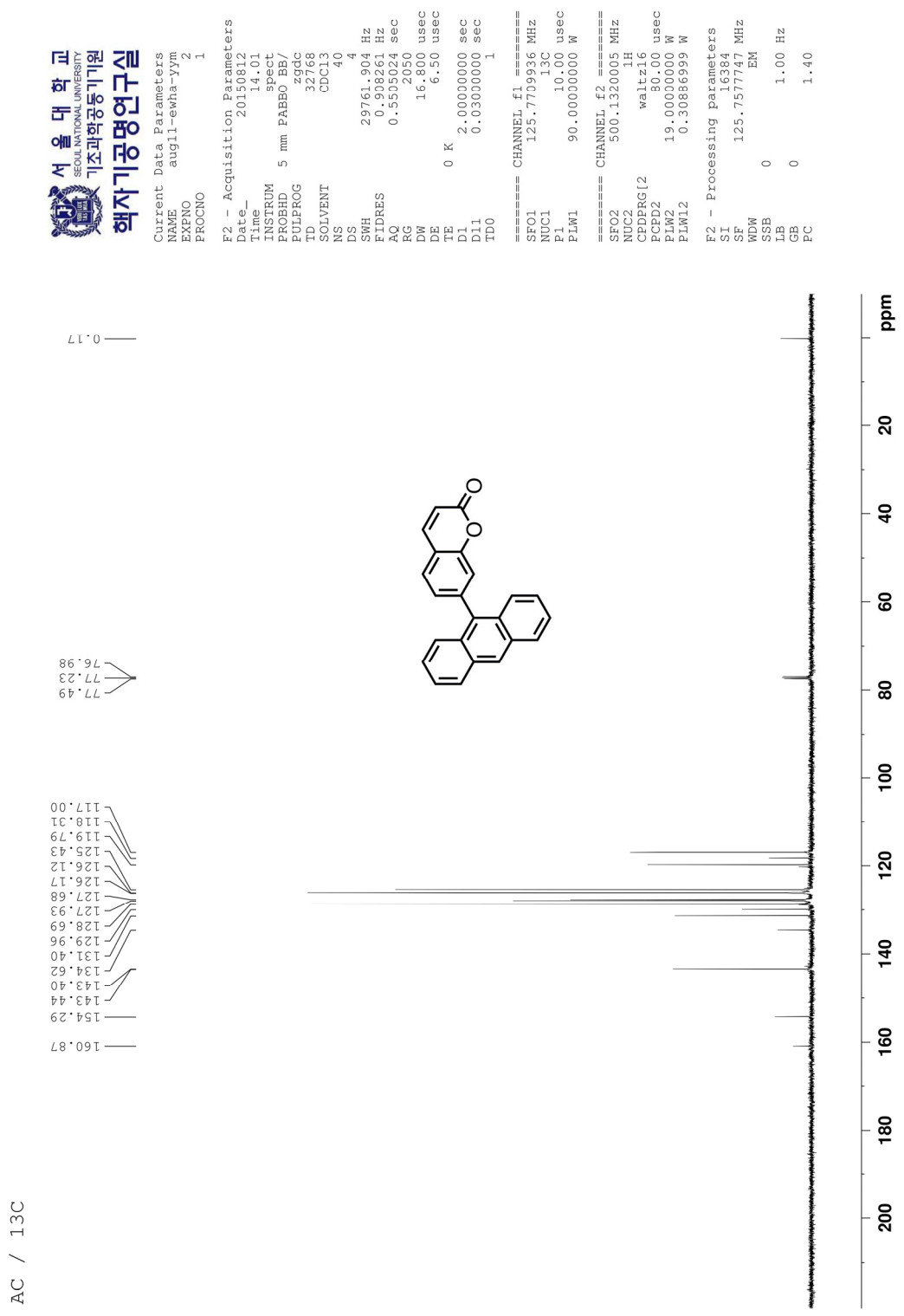

Fig. S18. $^{13}C\{^{1}H\}$ NMR spectrum of AC ($CDCl_3$, 126 MHz).

Table S2. Photophysical Data for PMMA Films Containing 10 wt % Coumarin Compounds

	10 wt % in PMMA				
	λ_{ems} (nm)	PLQY[a]	τ_{avg} (ns)[b]	k_r (10^7 s^{-1})[c]	k_{nr} (10^7 s^{-1})[d]
C	399	0	7.4	0	14
PC	402	0.019±0.0008	8.4	0.23	12
NC	407	0.027±0.007	1.9	1.4	51
AC	443	0.41±0.002	1.7	24	35

[a]Photoluminescence quantum yields determined absolutely by employing an integrating sphere. PMMA films containing 10 wt % 9,10-diphenylanthracene were used as the external standard (PLQY = 0.83±0.10). [b]Photoluminescence decay traces were monitored at the emission maximum for the polymer films after picosecond pulsed laser photoexcitation at 377 nm. The multiphasic decay traces were fit to a triexponential decay model. A weighted-average lifetime (τ_{avg}) was calculated using through $\tau_{avg} = (\Sigma a_i \cdot \tau_i^2)/(\Sigma a_i \cdot \tau_i)$ (i = 1–3). [c]Radiative rate constant, k_r = PLQY/τ_{obs}. [d]Non-radiative rate constant, k_{nr} = (1 − PLQY)/τ_{obs}.