Supporting Information

FDCA Bio-based Copolyester PBFA: Synthesis, Properties, and Fluorescence Regulation

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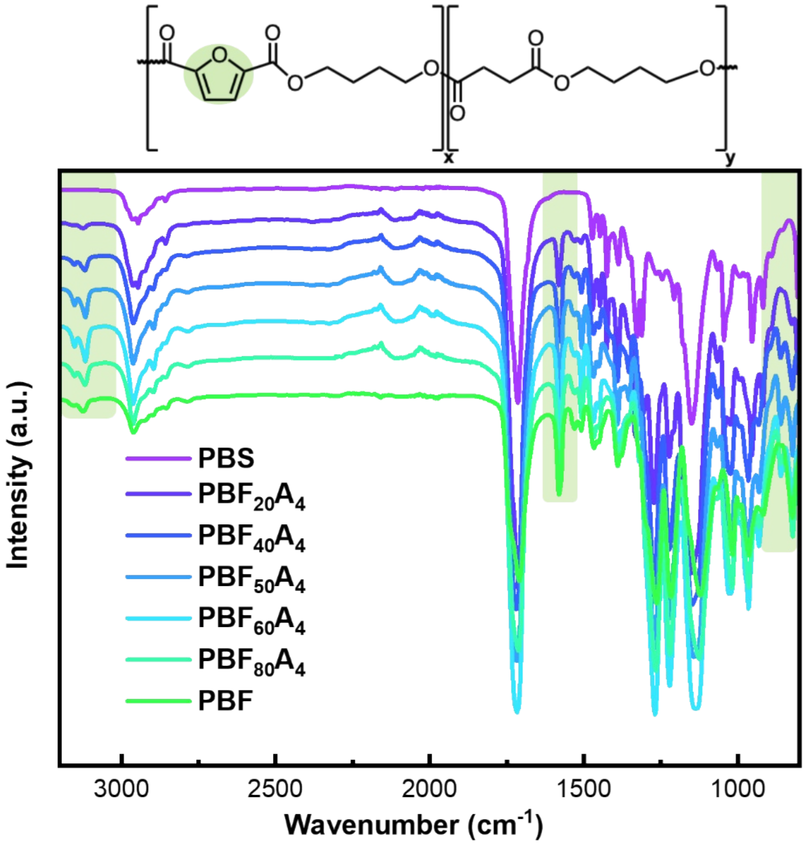

Fig. S1. ATR-FTIR spectra of PBFA$_4$.

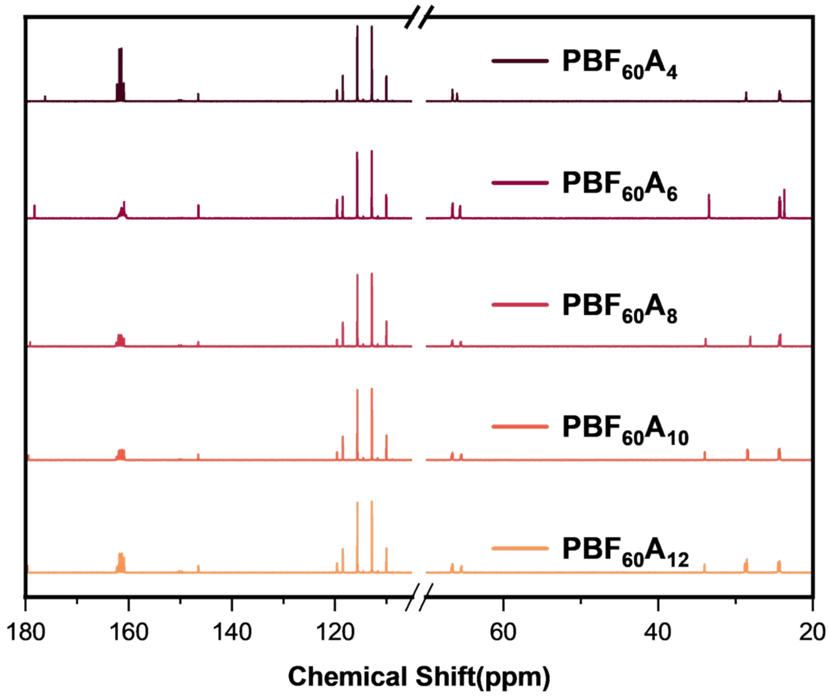

Fig. S2. **^{13}C-NMR spectra of PBF$_{60}$An.**

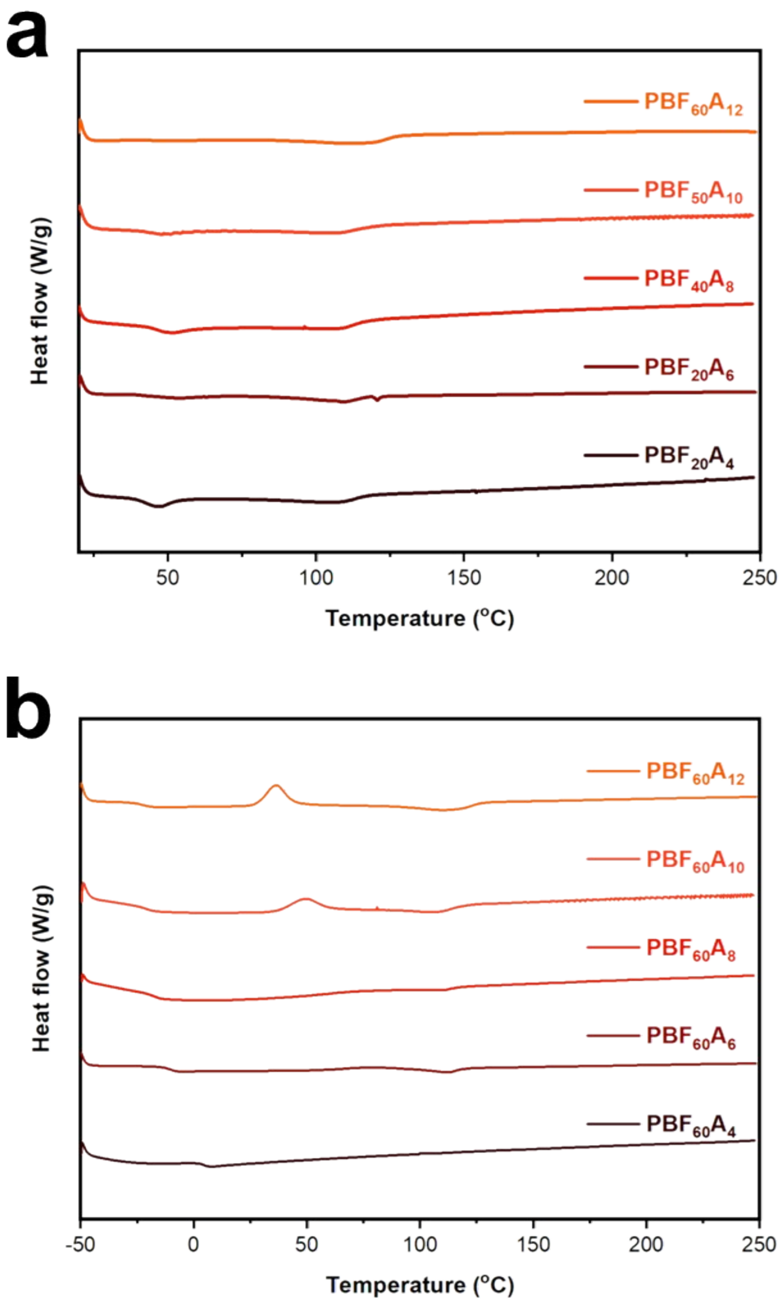

Fig. S3. DSC curves for PBF$_{60}$A$_{n}$. (a) Primary heating curve. **(b)** Secondary heating curve.

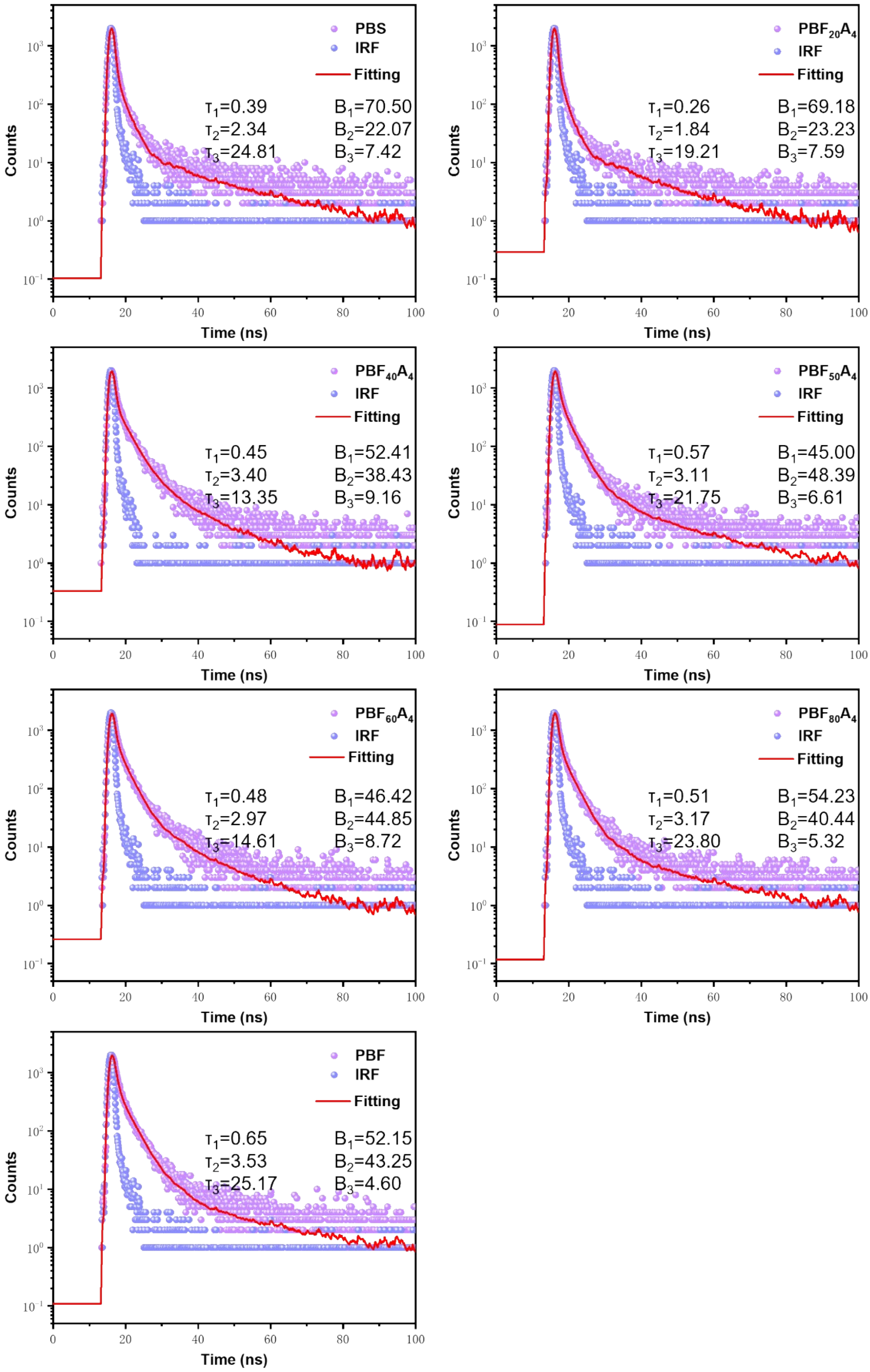

Fig. S4. Fluorescence lifetime fitting curves for PBF_xA_4.

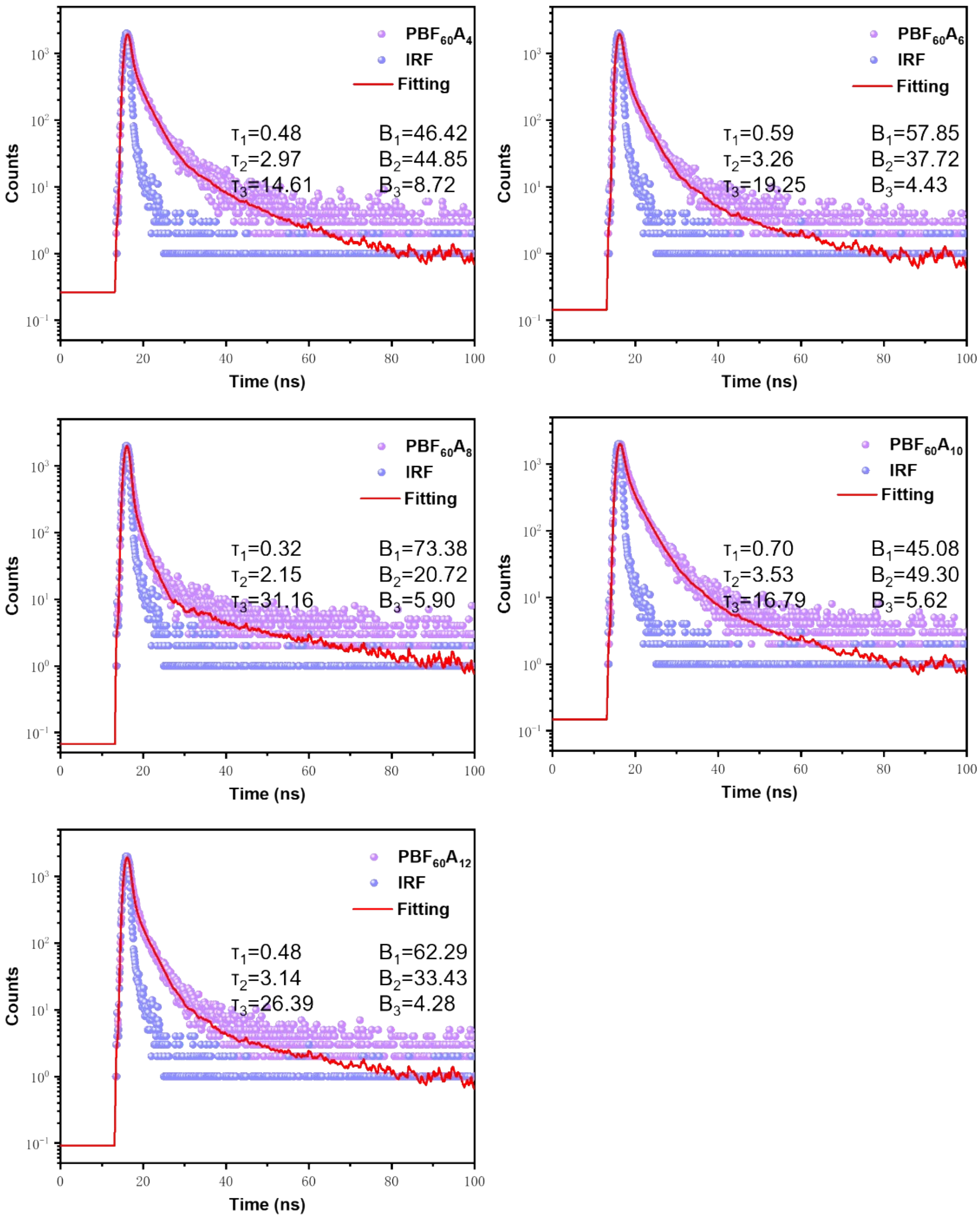

Fig. S5. Fluorescence lifetime fitting curves for $PBF_{60}A_n$.

Table S1. Fluorescence lifetime of PBFA.

Sample	τ_1	B_1	τ_2	B_2	τ_3	B_3	τ_{avg}
PBS	0.39	70.5	2.34	22.07	24.81	7.42	17.85
$PBF_{20}A_4$	0.26	69.18	1.84	23.23	19.21	7.59	13.96
$PBF_{40}A_4$	0.45	52.41	3.4	38.43	13.35	9.16	7.55
$PBF_{50}A_4$	0.57	45	3.11	48.39	21.75	6.61	11.28
$PBF_{60}A_4$	0.48	46.42	2.97	44.85	14.61	8.72	8.02
$PBF_{80}A_4$	0.51	54.23	3.17	40.44	23.8	5.32	12.16
PBF	0.65	52.15	3.53	43.25	25.17	4.6	11.50
$PBF_{60}A_6$	0.59	57.85	3.26	37.72	19.25	4.43	8.51
$PBF_{60}A_8$	0.32	73.38	2.15	20.72	31.16	5.9	23.15
$PBF_{60}A_{10}$	0.7	45.08	3.53	49.3	16.79	5.62	7.40
$PBF_{60}A_{12}$	0.48	62.29	3.14	33.43	26.39	4.28	13.41

The molecular weight and molecular weight distribution were determined using a Waters 2414 gel permeation chromatograph (GPC) system. The measurements were conducted at 35°C with chromatographic-grade chloroform as the mobile phase at a flow rate of 1.0 mL/min. A calibration curve was established using monodisperse polystyrene standards.

Table S2. Characterization of the molecular weight of PBFA.

Sample	[η]	M_n(g/mol)	M_w(g/mol)	PDI
PBA_4	1.12	32600	59000	1.81
$PBF_{20}A_4$	1.32	34900	75100	2.15
$PBF_{40}A_4$	1.16	27000	61200	2.27
$PBF_{50}A_4$	1.19	26500	61800	2.33
$PBF_{60}A_4$	1.18	27000	59500	2.20
$PBF_{80}A_4$	1.19	insol.	insol.	-
PBF	1.10	insol.	insol.	-

The intrinsic viscosity ([η]) measured in phenol/1,1,2,2-tetrachloroethane mixed solvent further confirms the successful synthesis of high-molecular-weight PBFA copolymers. The viscosity-average molecular weight (Mv) was determined by combining the measured [η] with the Mark-Houwink equation.

$$M_v = \left(\frac{[\eta]}{K}\right)^{\frac{1}{\alpha}}$$

Table S3. Viscosity-average molecular weight of PBFA.

Sample	K [a] ($\times 10^{-4}$ dL/g)	α [a]	[η] (dL/g)	M_v(g/mol)
PBA_4	2.8	0.77	1.12	47,000
$PBF_{20}A_4$	2.76	0.774	1.32	60,800
$PBF_{40}A_4$	2.72	0.778	1.16	50,200
$PBF_{50}A_4$	2.7	0.78	1.19	51,300
$PBF_{60}A_4$	2.68	0.782	1.18	50,500
$PBF_{80}A_4$	2.64	0.786	1.19	50,900
PBF	2.6	0.79	1.10	44,700

[a]The values of K and α for the homopolymer were extrapolated from literature data[1], and then linearly extrapolated to obtain the K and α values for PBFA.

Since the torque at the reaction endpoint was nearly identical, the intrinsic viscosity of the PBFA copolymers is very similar, suggesting their molecular weights should also be quite comparable. For subsequent thermal, mechanical, and fluorescence tests, the influence of molecular weight differences can be essentially neglected.

Supplementary Methods

Crystallinity-tunable films

The PBFA pellets were sandwiched between two polyimide films and hot-pressed at 180°C under 500 kgf pressure for 3 minutes using an IDM-L0003 hot press. Immediately after pressing, the samples were quenched in liquid nitrogen for 10 seconds to freeze the microstructure, followed by isothermal annealing at the predetermined crystallization temperature (based on DSC analysis) for varying durations to investigate crystallization behavior. All annealing processes terminated by rapid liquid nitrogen quenching to preserve the developed crystalline structures.

Sample	Annealing temperature(°C)	Annealing time(min)
PBF60A4-1	-	0
$PBF_{60}A_4$-2	70	10
$PBF_{60}A_4$-3	70	20
$PBF_{80}A_4$-1	-	0
$PBF_{80}A_4$-2	100	10
$PBF_{80}A_4$-3	100	20
$PBF_{80}A_4$-4	100	30

Fluorescence lifetime test [2]

The formula for calculating the average fluorescence lifetime of the copolyester film is as follows:

$$\tau_{avg} = \frac{\left(B_1{\tau_1}^2 + B_2{\tau_2}^2 + B_3{\tau_3}^2\right)}{\left(B_1\tau_1 + B_2\tau_2 + B_3\tau_3\right)} \tag{1}$$

τ_{avg} represents the average fluorescence lifetime of the material, and B_1, B_2, and B_3 represent the percentages of each τ.

Abbreviation list

PBFA: Copolyesters of aliphatic dicarboxylic acid, furandicarboxylic acid, and 1,4-butanediol

FDCA: 2,5-Furandicarboxylic acid

TPA: terephthalic acid

CTE: clustering-triggered emission

PEF: poly(ethylene furandicarboxylate)

PBF: poly(butylene furandicarboxylate)

PPF: poly(propylene furandicarboxylate)

AIE: Aggregation-induced emission

NTIL: Non-traditional intrinsic luminescence

PBS: Polybutylene Succinate

BDO: 1,4-butanediol

PEFA: Copolyesters of aliphatic dicarboxylic acid, furandicarboxylic acid, and ethylene glycol

Supplementary References

(1) Lv, X.; Luo, F.; Zheng, L.; Niu, R.; Liu, Y.; Xie, Q.; Song, D.; Zhang, Y.; Zhou, T.; Zhu, S. Biodegradable poly(butylene succinate-co-butylene furandicarboxylate): Effect of butylene furandicarboxylate unit on thermal, mechanical, and ultraviolet shielding properties, and biodegradability. *J. Appl. Polym. Sci.* **2022**, *139* (45), e53122, Article. DOI: 10.1002/app.53122.

(2) Das, D.; Dutta, R. K. Photoluminescence lifetime based nickel ion detection by glutathione capped CdTe/CdS core-shell quantum dots. *J. Photochem. Photobiol. A-Chem.* **2021**, *416*, 9, Article. DOI: 10.1016/j.jphotochem.2021.113323.