Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting information

Mechanofluorochromism of Pyrene–Derived Amidophosphonates

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Table S1. Crystallographic parameters of the pyrene-derived amidophosphonates **AP1-3**.

	AP1	**AP2**	**AP3**
Chemical formula	$C_{23}H_{24}NO_4P$	$C_{25}H_{28}NO_4P$	$C_{28}H_{26}NO_4P$
Formula weight	409.40	437.45	471.47
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*P* $2_1/c$ (#14)	*C* 2/*c* (#15)	*P* -1 (#2)
a/Å	14.1914(5)	26.8408(13)	9.7414(5)
b/Å	9.0659(3)	9.9974(5)	10.2898(5)
c/Å	16.0033(5)	17.4578(8)	13.4571(6)
α/deg	90.000	90.000	110.2840(10)
β/deg	101.488(2)	110.5060(10)	109.5130(10)
γ/deg	90.000	90.000	90.7320(10)
Volume/Å^3	2017.70(12)	4387.8(4)	1179.90(10)
Z / *Z'*	4 / 1	8 / 1	2 / 1
d_{calc}/g cm^{-3}	1.348	1.324	1.327
Temperature/K	100(1)	100(1)	100(1)
μ (Cu Kα)/mm^{-1}	1.458	1.374	1.323
max 2*θ*/deg	65.304	66.654	66.716
Reflections collected	20695	36707	29926
Reflections unique	3458	3865	4175
Refl. obs. (I>2σ(I))	2759	3764	4071
R_{int}	0.0601	0.0314	0.0302
Parameters	265	295	311
$R_1(I>2\sigma(I))$	0.0473	0.0330	0.0377
wR_2 (all data)	0.1147	0.0856	0.1017
GOF	1.037	1.048	1.074
Largest diff. peak and hole (e..Å^{-3})	0.416 ; -0.281	0.339 ; -0.382	0.469 ; -0.388

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$

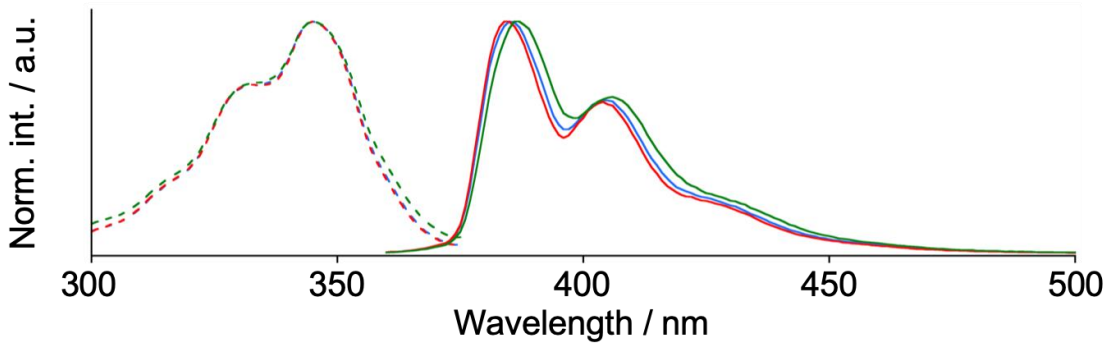

Figure S1. Normalized absorption/emission spectra of a) **AP1** (blue), b) **AP2** (red) and c) **AP3** (green) in 10^{-6} M $CHCl_3$ solution (λ_{ex} = 340 nm for emission spectra).

Table S2. Emission lifetimes τ and their final chi-square values X_R^2 of **AP1-3** in 10^{-6} M $CHCl_3$ solution (λ_{ex} = 360 nm, λ_{em} = 390 nm).

Sample	Lifetime τ / ns	Final chi-square X_R^2
AP1	10.4	1.07
AP2	10.9	1.09
AP3	9.3	1.10

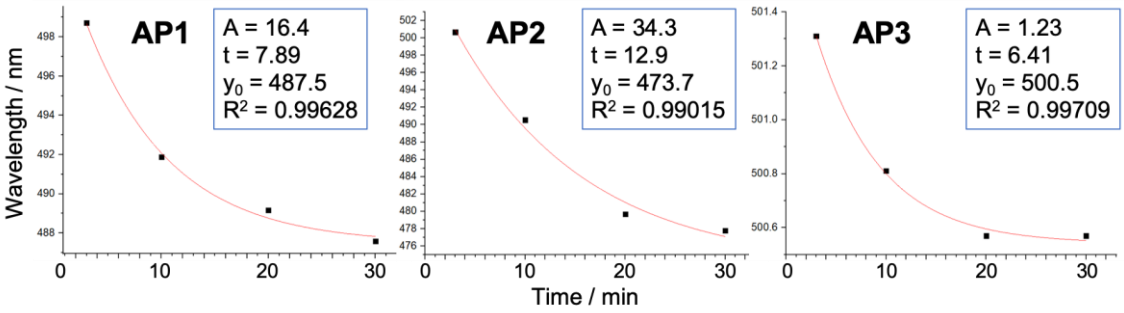

Figure S2. Exponential-decay fitting analysis of time-dependent λ_{mean} of **AP1-3** (values inset correspond to a function: $y = A*\exp(-x/t) + y_0$).

Table S3. Emission lifetimes τ, corresponding normalized pre-exponential factors a and fractions of intensity f of **AP1-3**[a] (λ_{ex} = 360 nm, λ_{em} = 400/430/460 nm for pristine **AP1** and **AP2**, λ_{em} = 420/450/480 nm for pristine **AP3**, λ_{em} = 450, 480 and 510 nm for all ground form).

Sample	τ_1 / ns (a_1, f_1)	τ_2 / ns (a_2, f_2)	τ_3 / ns (a_3, f_3)	τ_4 / ns (a_4, f_4)	Global chi-square χ_R^2
AP1 pristine	31	15	6.0	1.0	1.00
λ_{em} = 400 nm	(0.02, 0.06)	(0.24, 0.43)	(0.70, 0.50)	(0.04, 0.01)	
λ_{em} = 430 nm	(0.15, 0.40)	(0.24, 0.29)	(0.61, 0.31)	(−0.25, −0.02)	
λ_{em} = 460 nm	(0.46, 0.72)	(0.27, 0.20)	(0.28, 0.08)	(−0.34, −0.02)	
AP1 ground	62	32	7.0	-	1.09
λ_{em} = 450 nm	(0.13, 0.30)	(0.51, 0.60)	(0.36, 0.10)	-	
λ_{em} = 480 nm	(0.23, 0.42)	(0.58, 0.54)	(0.18, 0.04)	-	
λ_{em} = 510 nm	(0.15, 0.28)	(0.77, 0.71)	(0.08, 0.02)	-	
AP2 pristine	44	21	5.3	1.1	0.97
λ_{em} = 400 nm	(0.01, 0.10)	(0.09, 0.39)	(0.38, 0.40)	(0.51, 0.11)	
λ_{em} = 430 nm	(0.11, 0.33)	(0.33, 0.47)	(0.56, 0.20)	(−0.02, 0.00)	
λ_{em} = 460 nm	(0.23, 0.47)	(0.49, 0.46)	(0.27, 0.07)	(−0.40, −0.02)	
AP2 ground	50	26	5.2	-	1.07
λ_{em} = 450 nm	(0.28, 0.54)	(0.40, 0.40)	(0.31, 0.06)	-	
λ_{em} = 480 nm	(0.36, 0.56)	(0.52, 0.42)	(0.12, 0.02)	-	
λ_{em} = 510 nm	(0.46, 0.66)	(0.43, 0.32)	(0.10, 0.02)	-	
AP3 pristine	25	7.0	2.0	0.48[b]	0.94
λ_{em} = 420 nm	(0.05, 0.33)	(0.08, 0.15)	(0.88, 0.51)	(−0.03, 0.00)	
λ_{em} = 450 nm	(0.11, 0.53)	(0.11, 0.16)	(0.78, 0.31)	(−0.97, −0.09)	
λ_{em} = 480 nm	(0.22, 0.69)	(0.18, 0.16)	(0.60, 0.15)	(−0.62, −0.04)	
AP3 ground	46	22	4.2	-	0.95
λ_{em} = 450 nm	(0.22, 0.49)	(0.41, 0.44)	(0.38, 0.08)	-	
λ_{em} = 480 nm	(0.39, 0.61)	(0.49, 0.37)	(0.13, 0.02)	-	
λ_{em} = 510 nm	(0.48, 0.65)	(0.52, 0.35)	(0.00, 0.00)	-	

[a] Pre-exponential factors and fractures of intensity were normalized by the sum of positive components. [b] Since the τ_4 of **AP3** pristine is close to the instrumental response function, the obtained values include relatively large errors. The error analysis was performed on the discrete fittings, and the τ_4 values were found to include 35-50% errors (0.63 ± 0.31 and 0.53 ± 0.19 ns for λ_{em} = 450 and 480 nm, respectively).

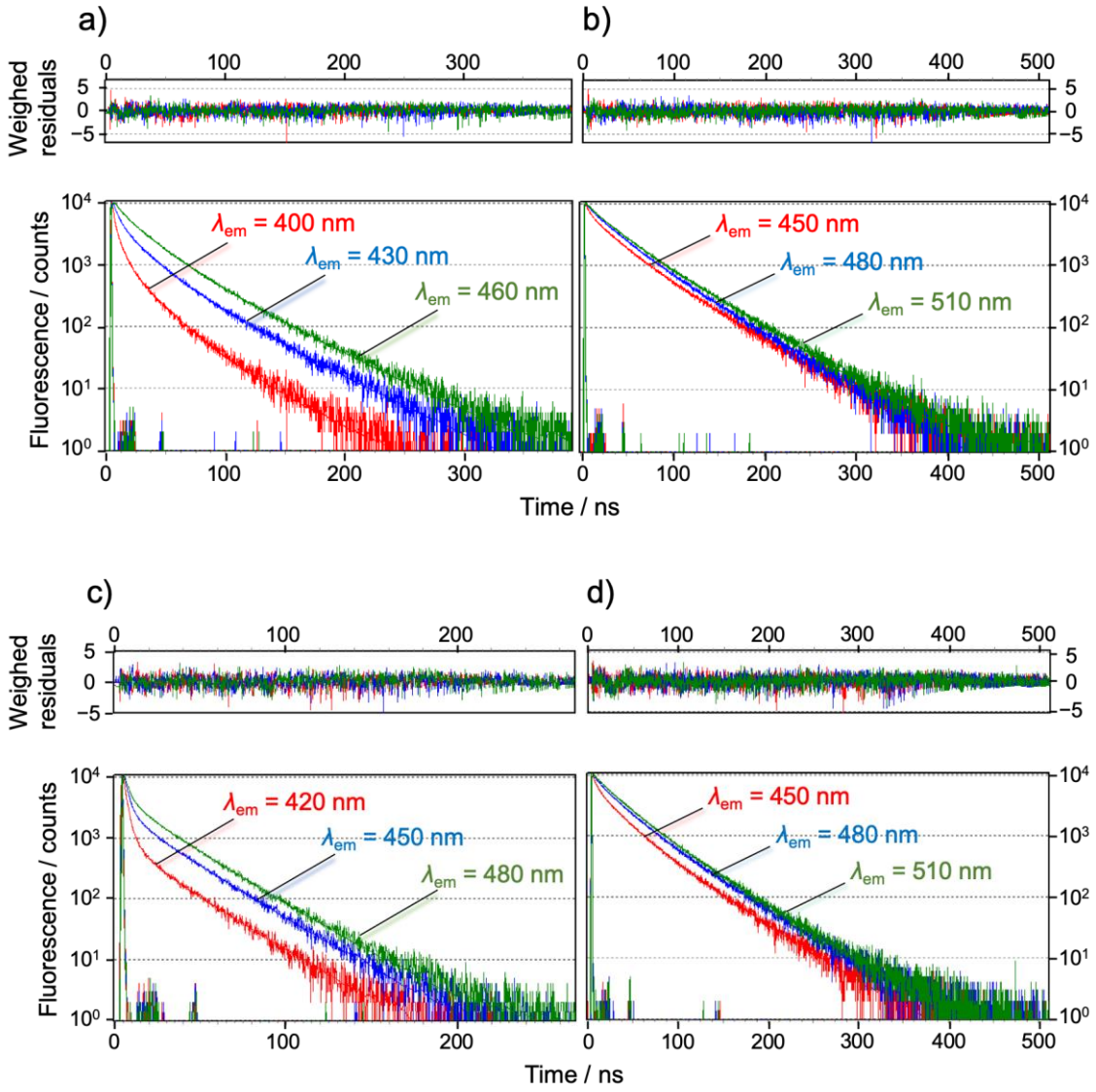

Figure S3. Fluorescence decay curves of a) **AP2** pristine, b) **AP2** ground, c) **AP3** pristine and d) **AP3** ground forms recorded in solid state with multiexponential fitting and weighted residuals.

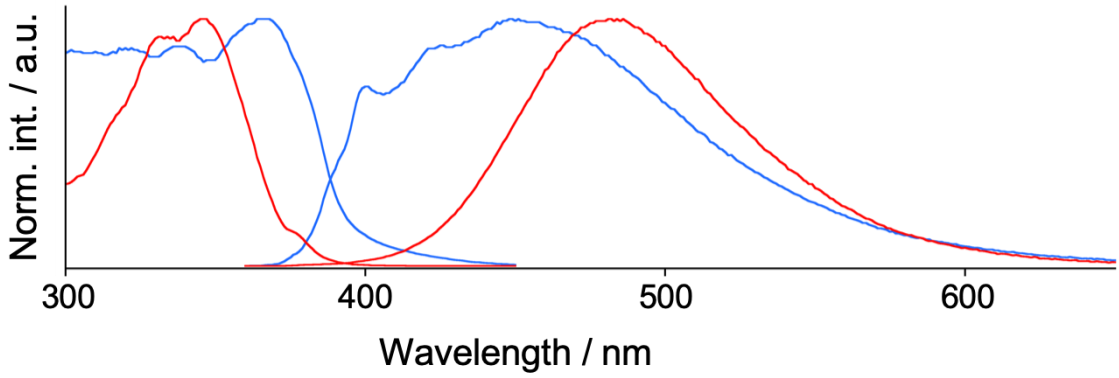

Figure S4. Excitation/emission spectra of **AP-H** in solid state (λ_{ex} = 340 nm, λ_{obs} = 480 nm, blue: pristine, red: ground form).