Electronic Supplementary Information (ESI)

Flexible-Color Tuning and White-Light Emission in Three-, Four-, and Five-component Host/Guest Co-crystals by Charge–Transfer Emissions as well as Effective Energy Transfers

Toshikazu Ono[1,2]*, Yoshio Hisaeda[1]*

1. Department of Chemistry and Biochemistry, Graduate School of Engineering, Center for Molecular Systems (CMS), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395 (Japan).
2. Japan Science and Technology Agency (JST)-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012 (Japan).

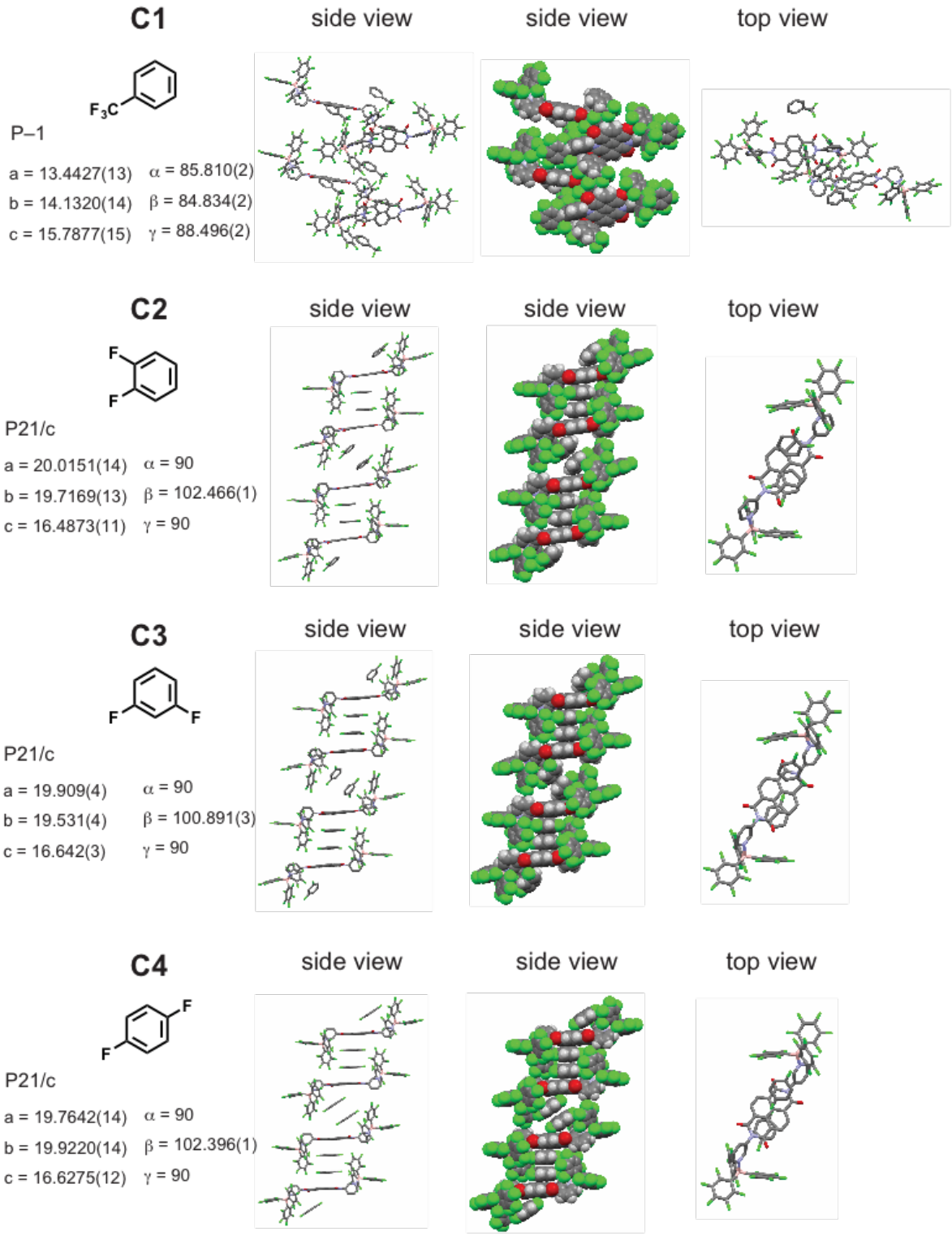


Fig. S1 Crystal structures of **C1–C4**.

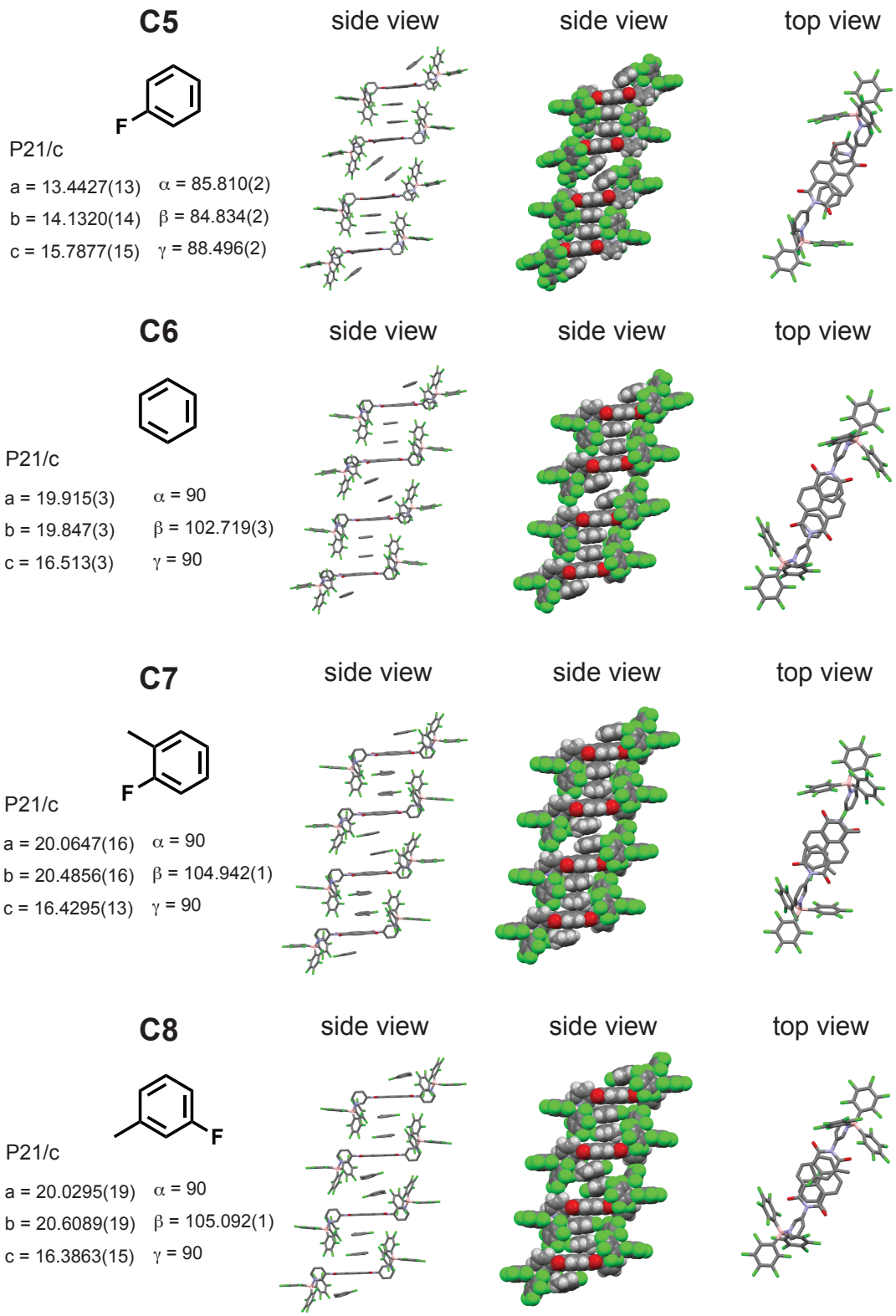


Fig. S2 Crystal structures of **C5–C8**.

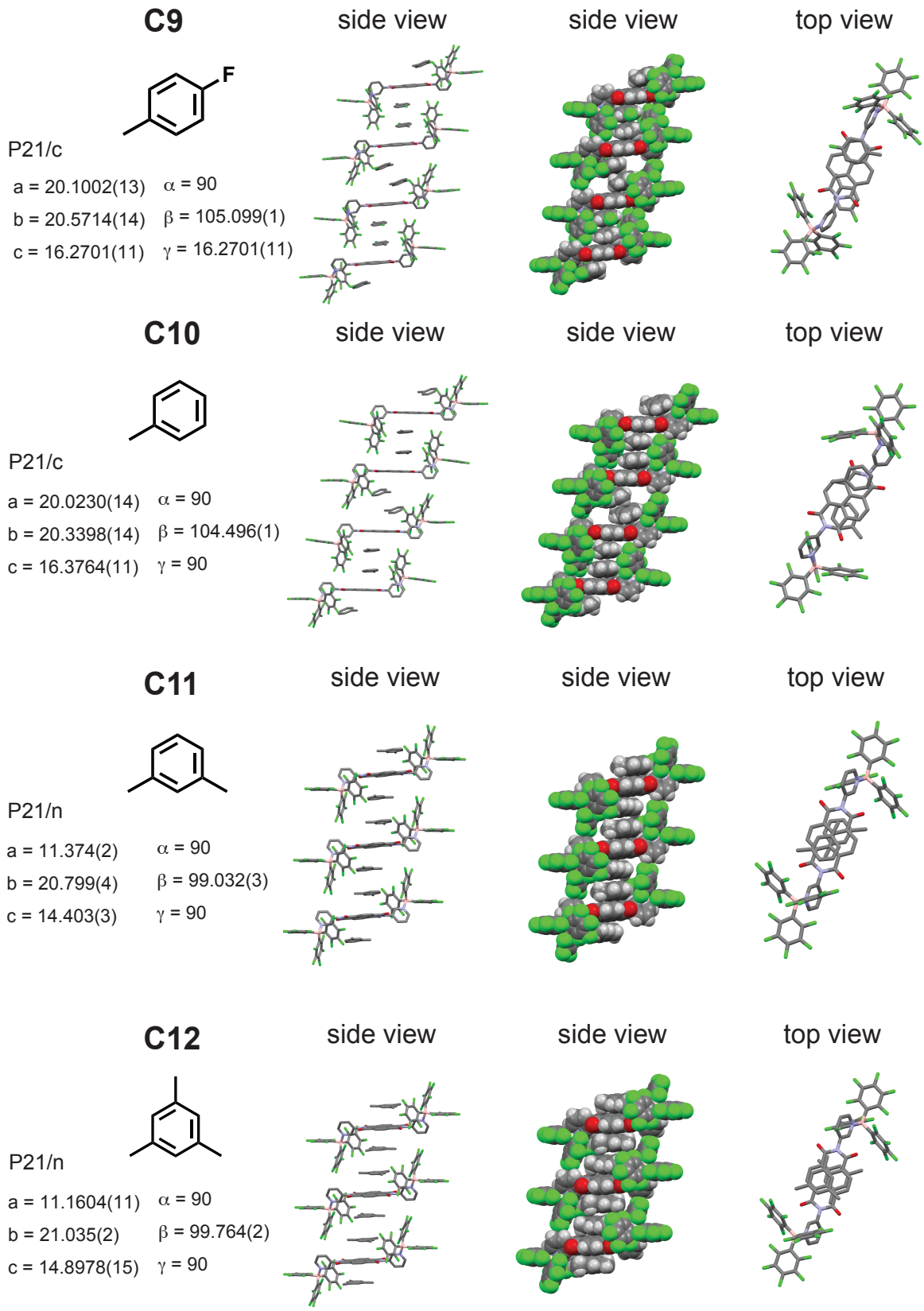


Fig. S3 Crystal structures of **C9–C12**.

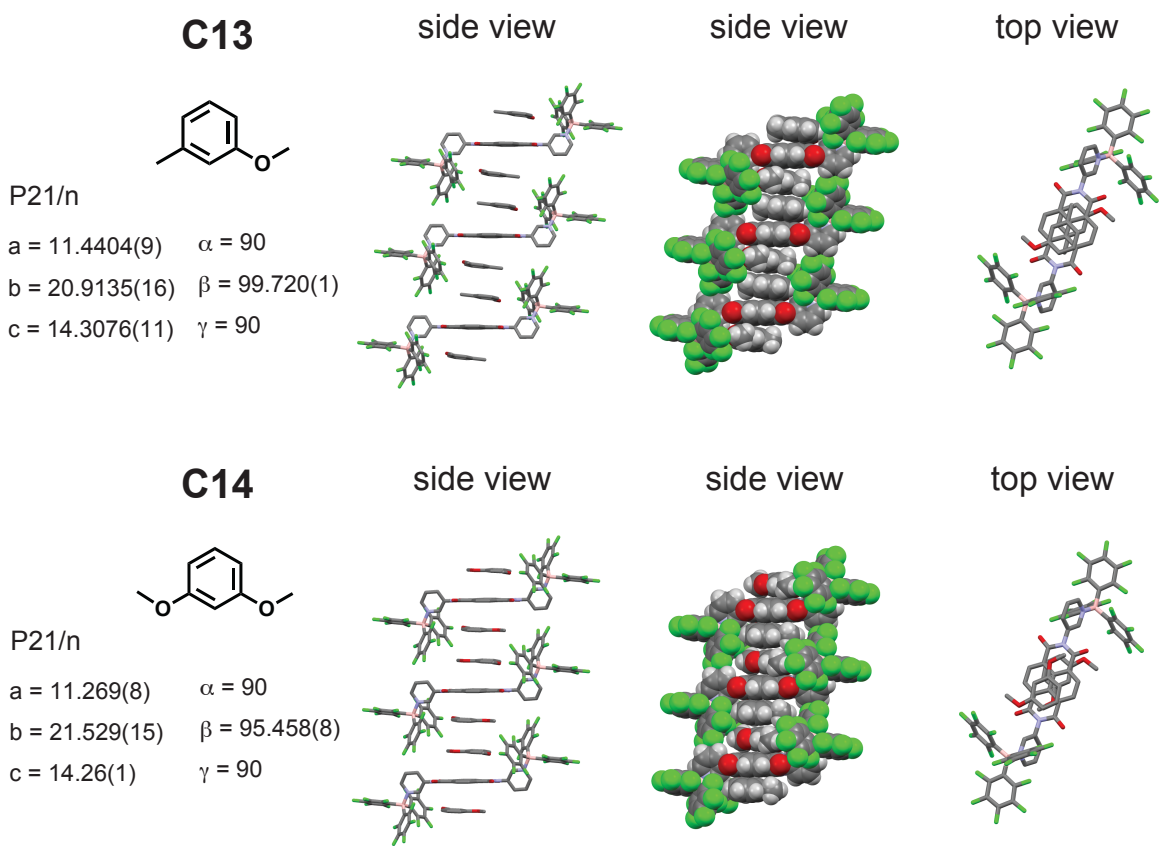
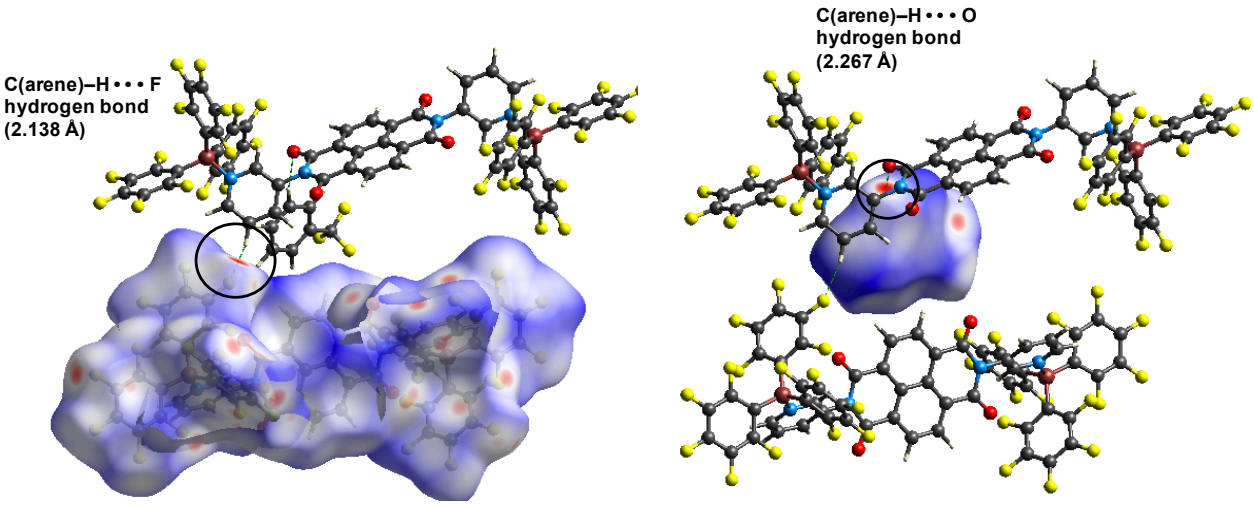
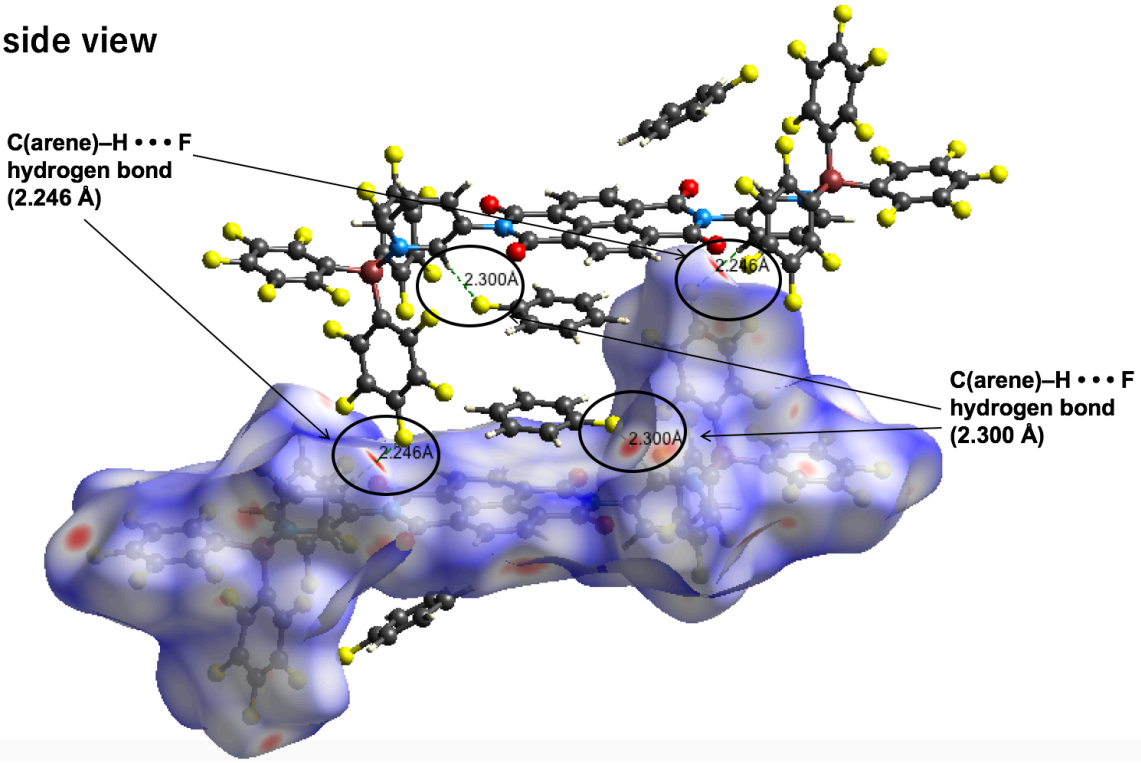


Fig. S4 Crystal structures of **C13–C14**.

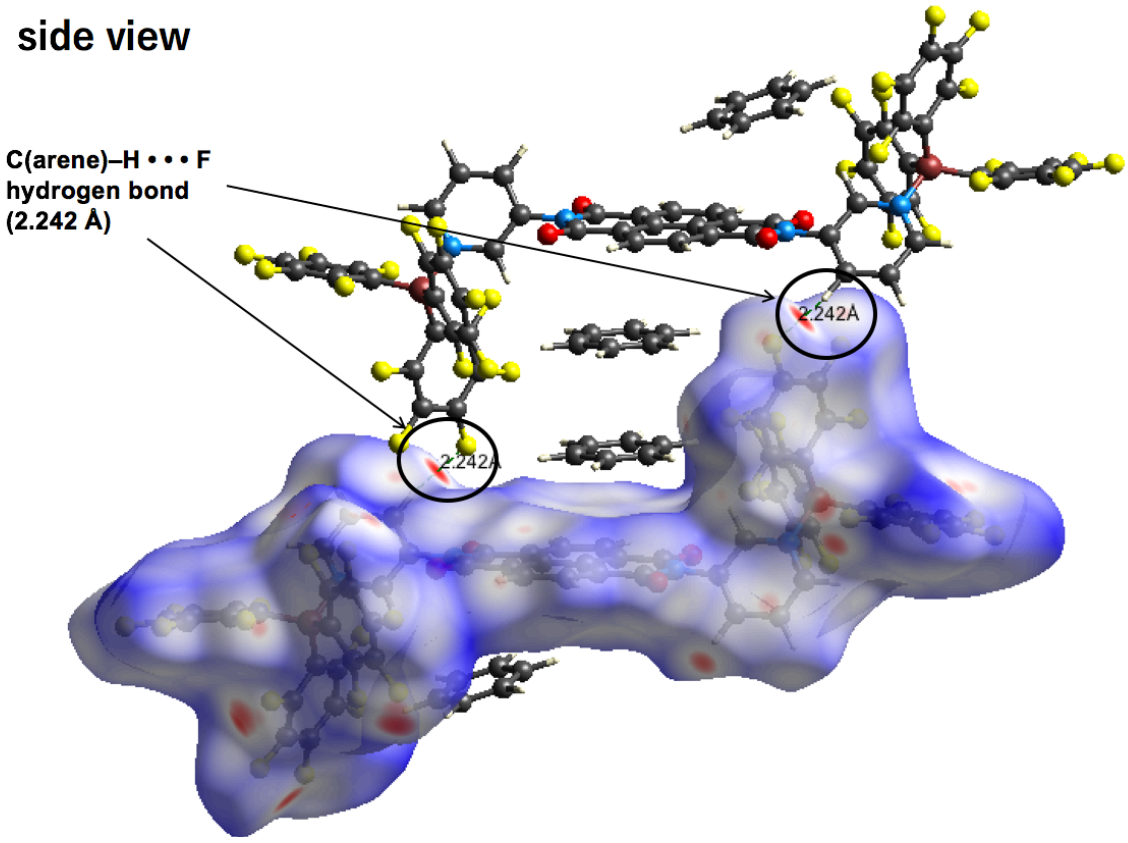
C1



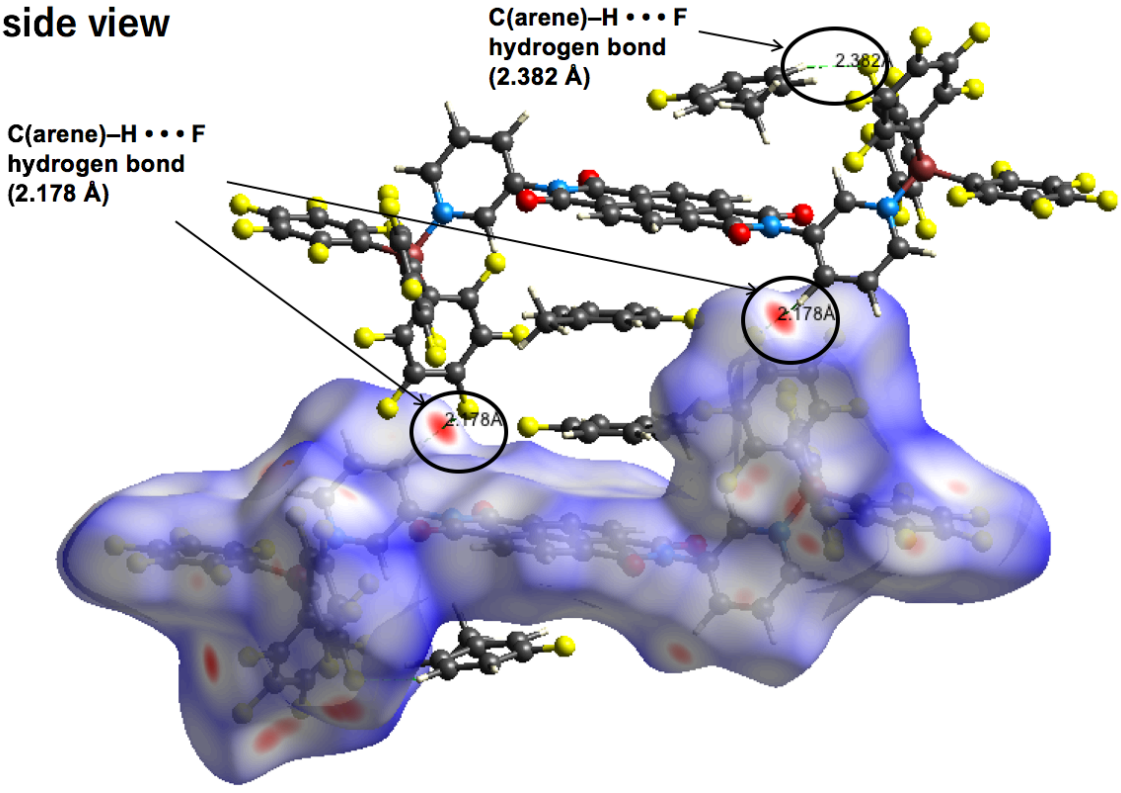
C5 side view



C6 side view



C8 side view



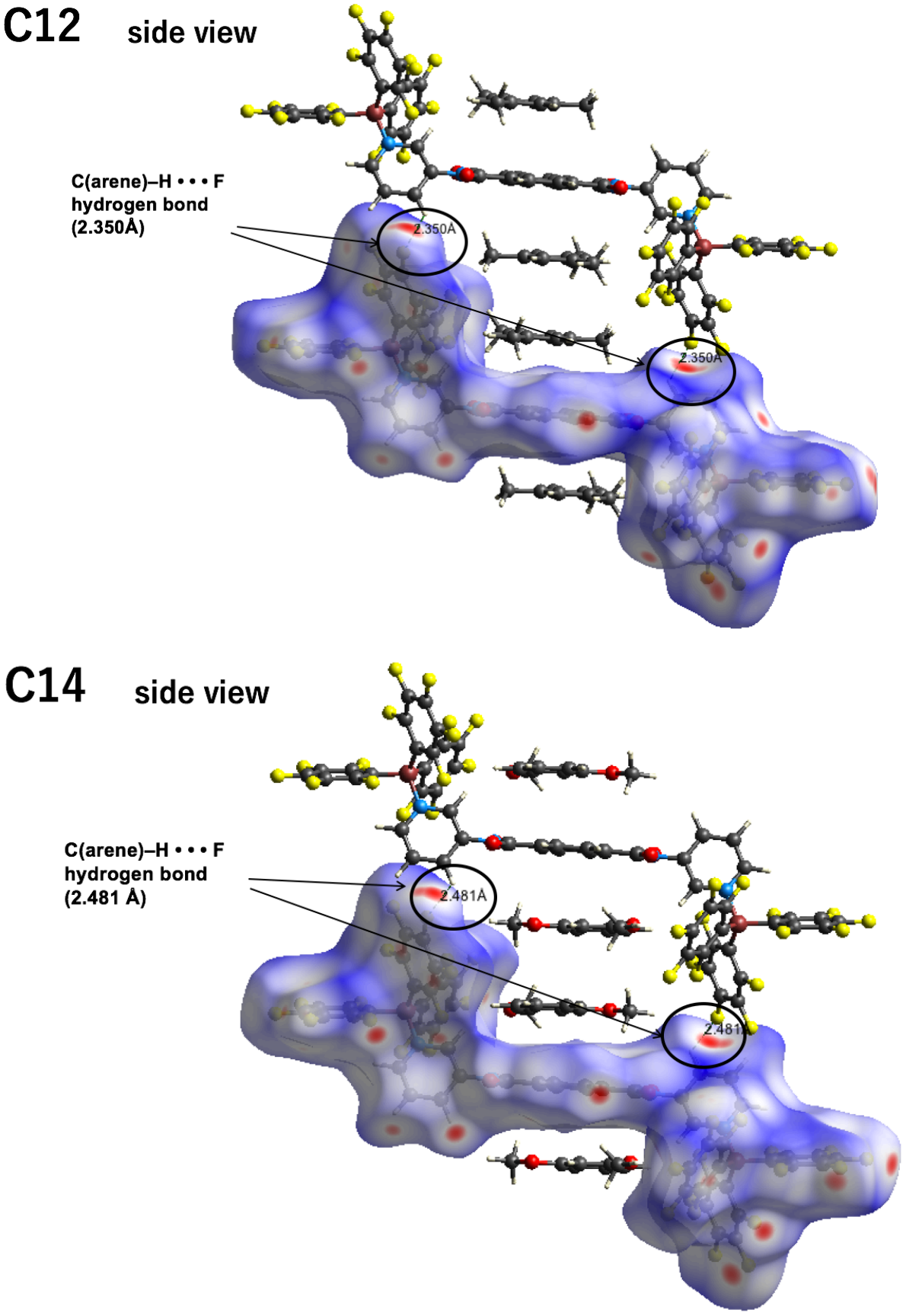


Fig. S5 Hirshfeld surface analysis of **C1, C5, C6, C8, C12,** and **C14**.

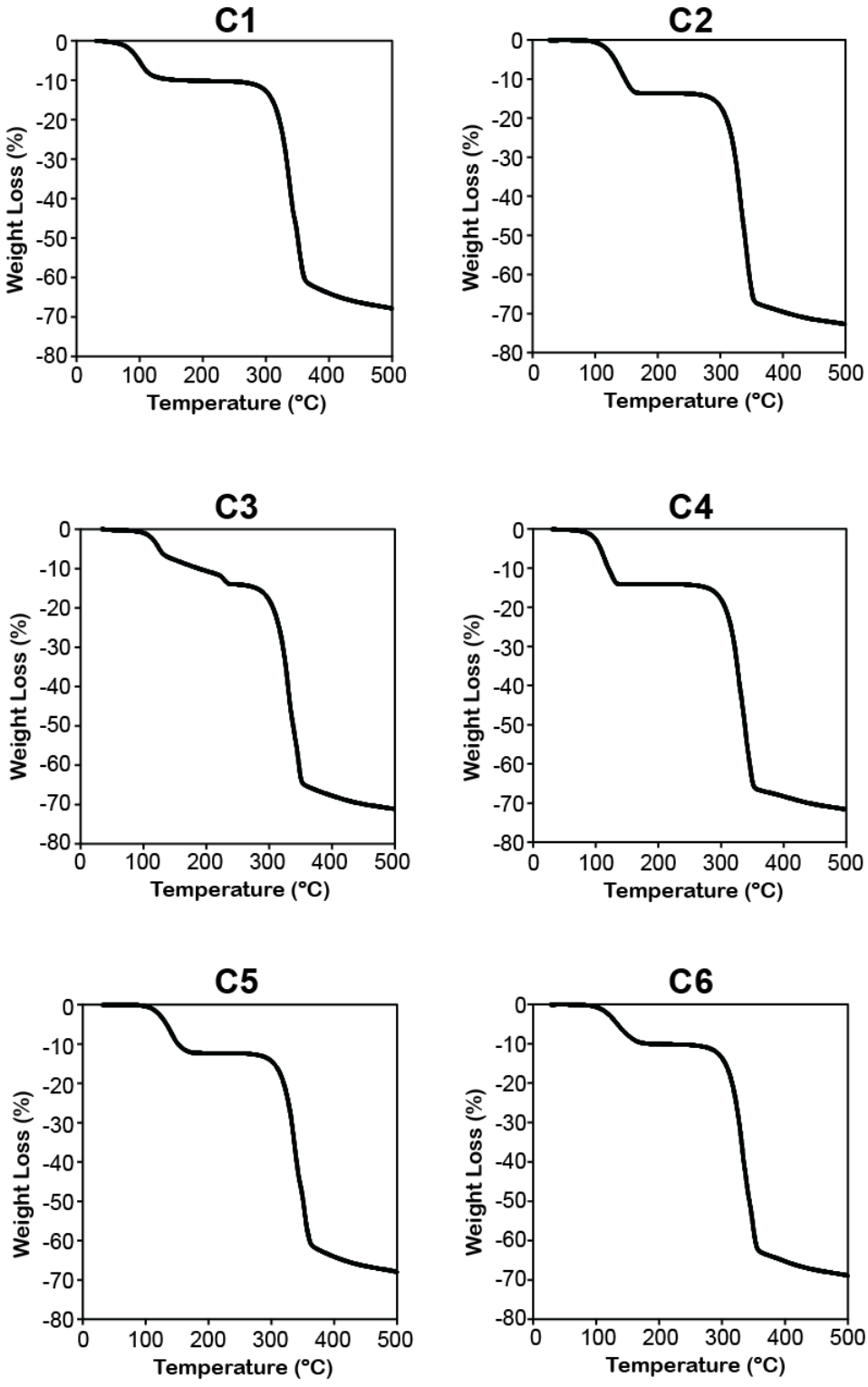


Fig. S6 TGA of **C1–C6**. The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

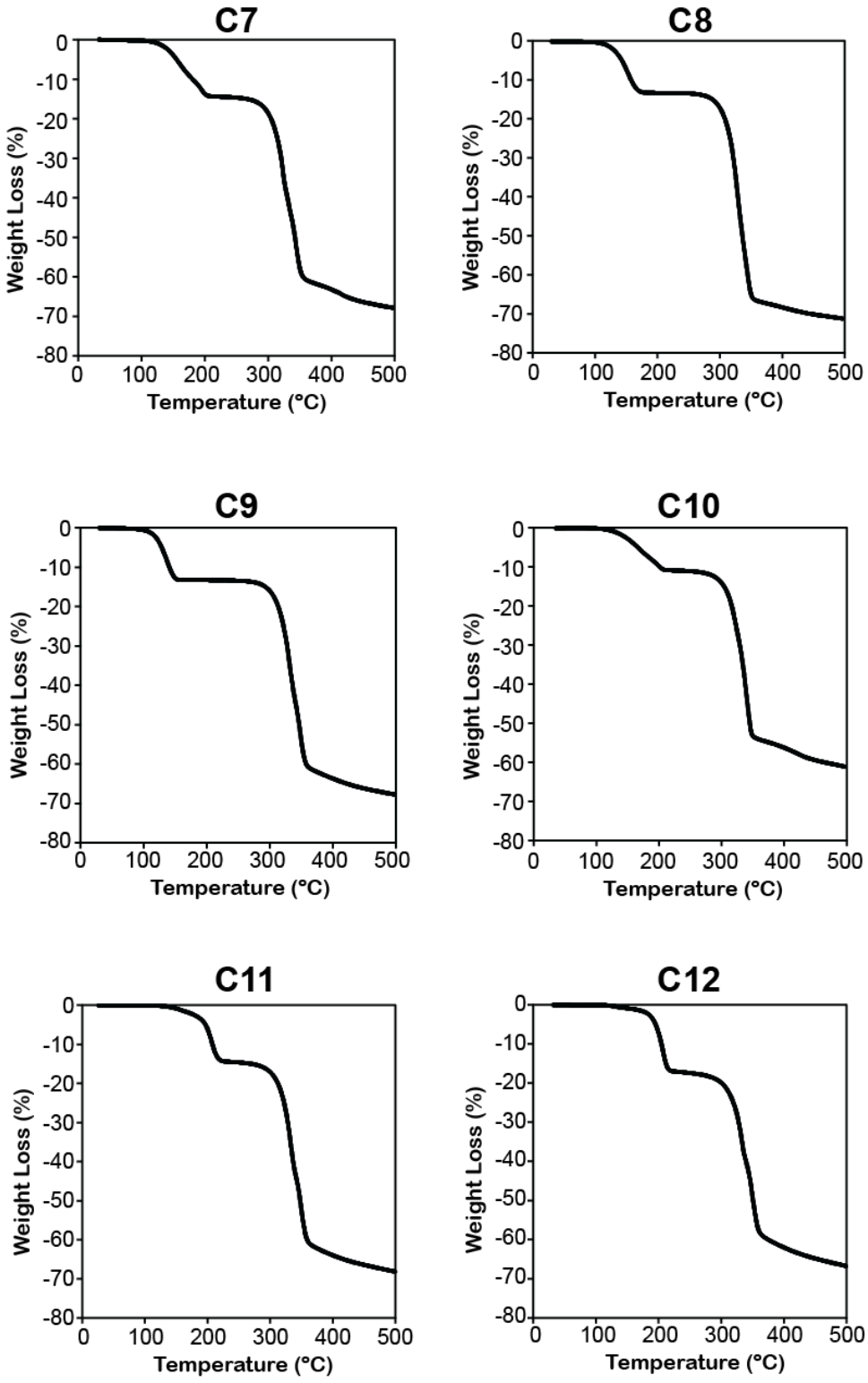


Fig. S7 TGA of **C7**–**C12**. The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

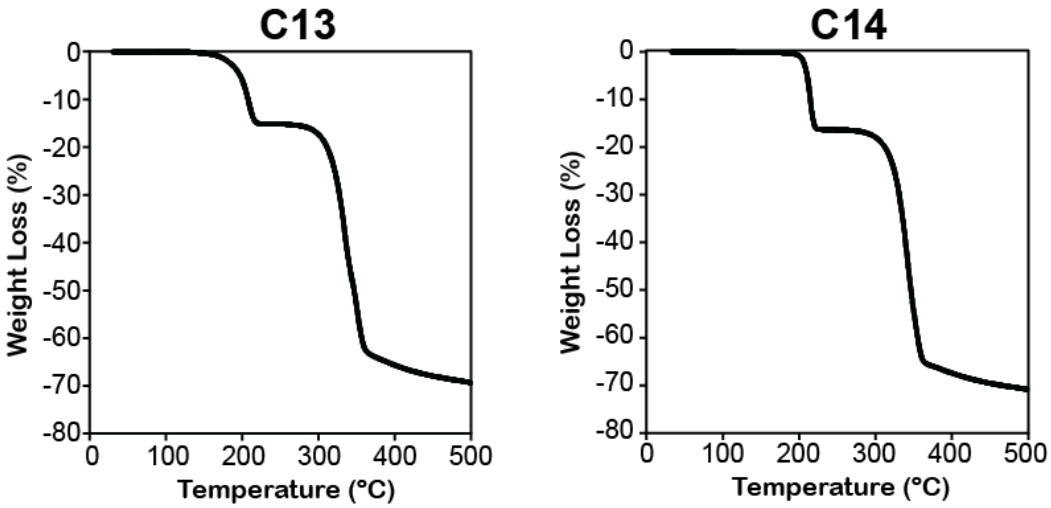


Fig. S8 TGA of **C13**–**C14**. The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

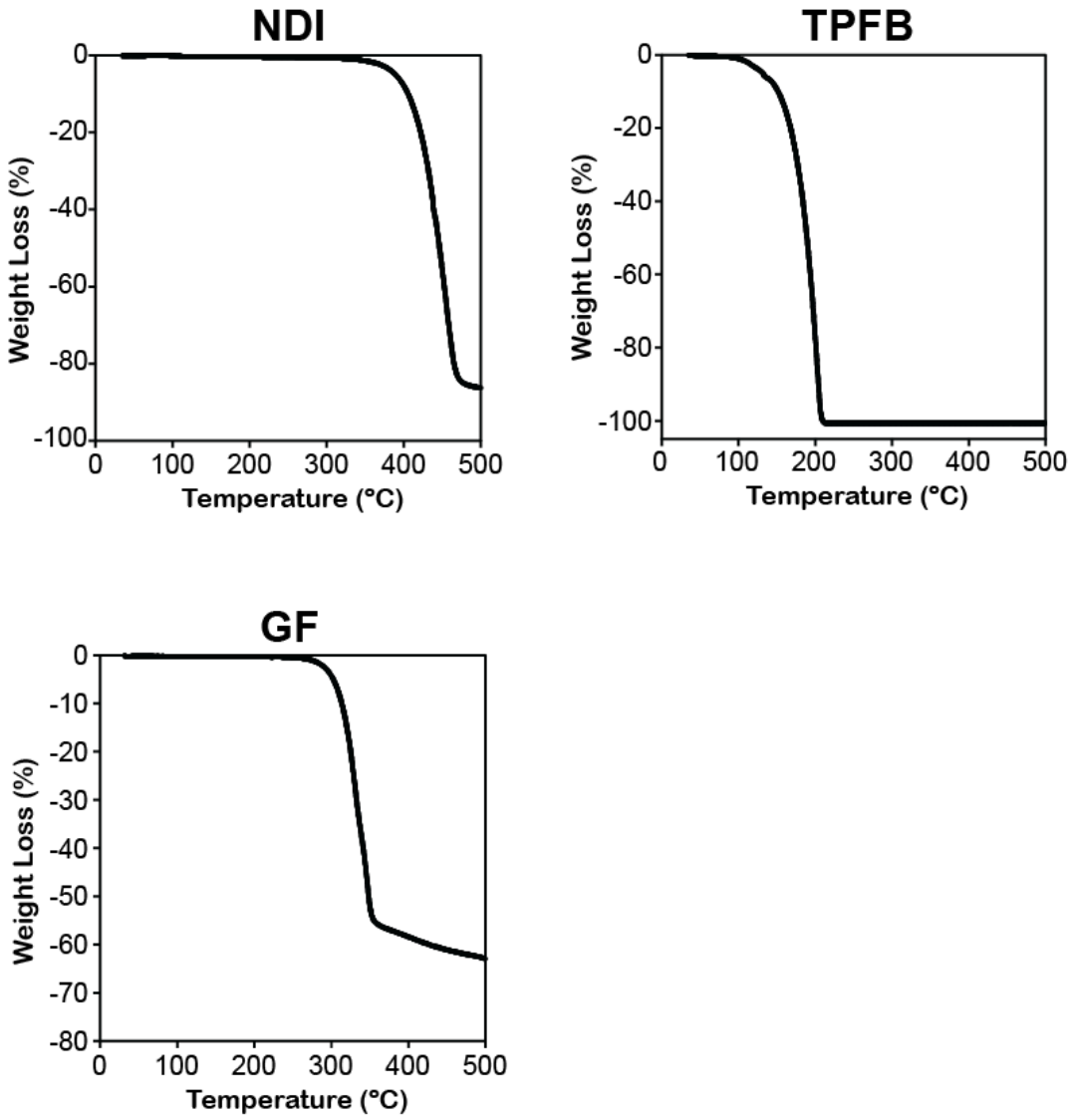


Fig. S9 TGA of NDI, TPFB, **GF.** The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

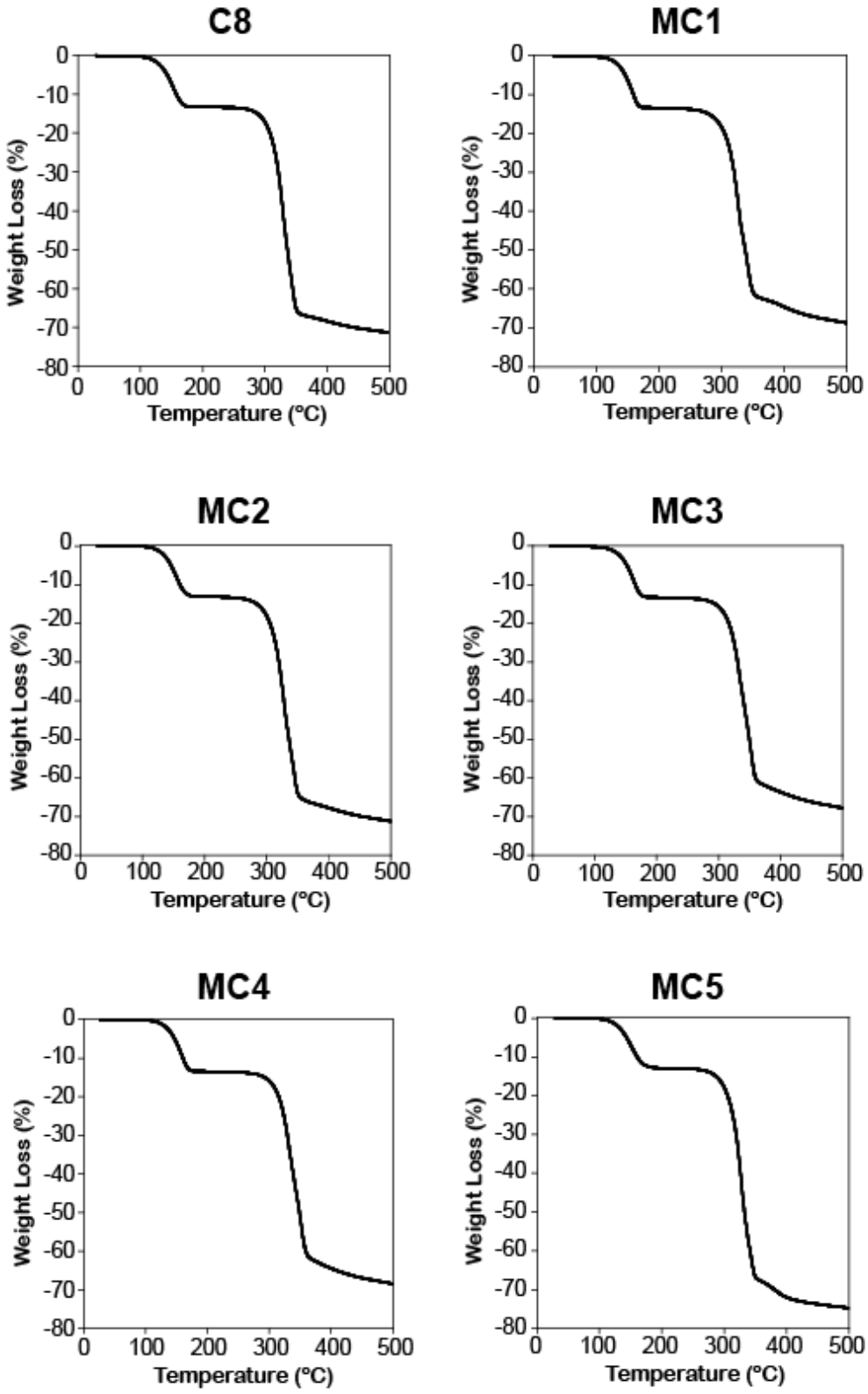


Fig. S10 TGA of **C8** and **MC1**–**MC5**. The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

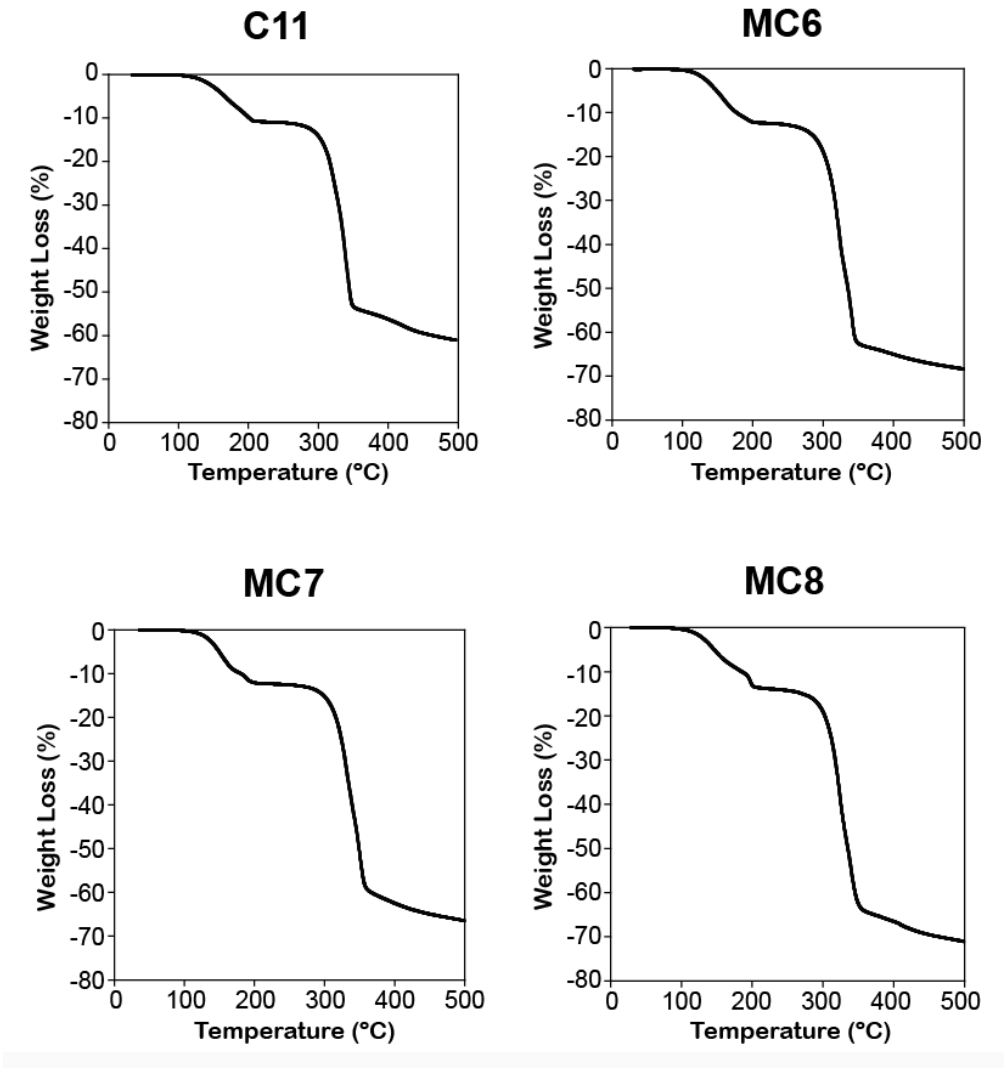


Fig. S11 TGA of **C11** and **MC6–MC8**. The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

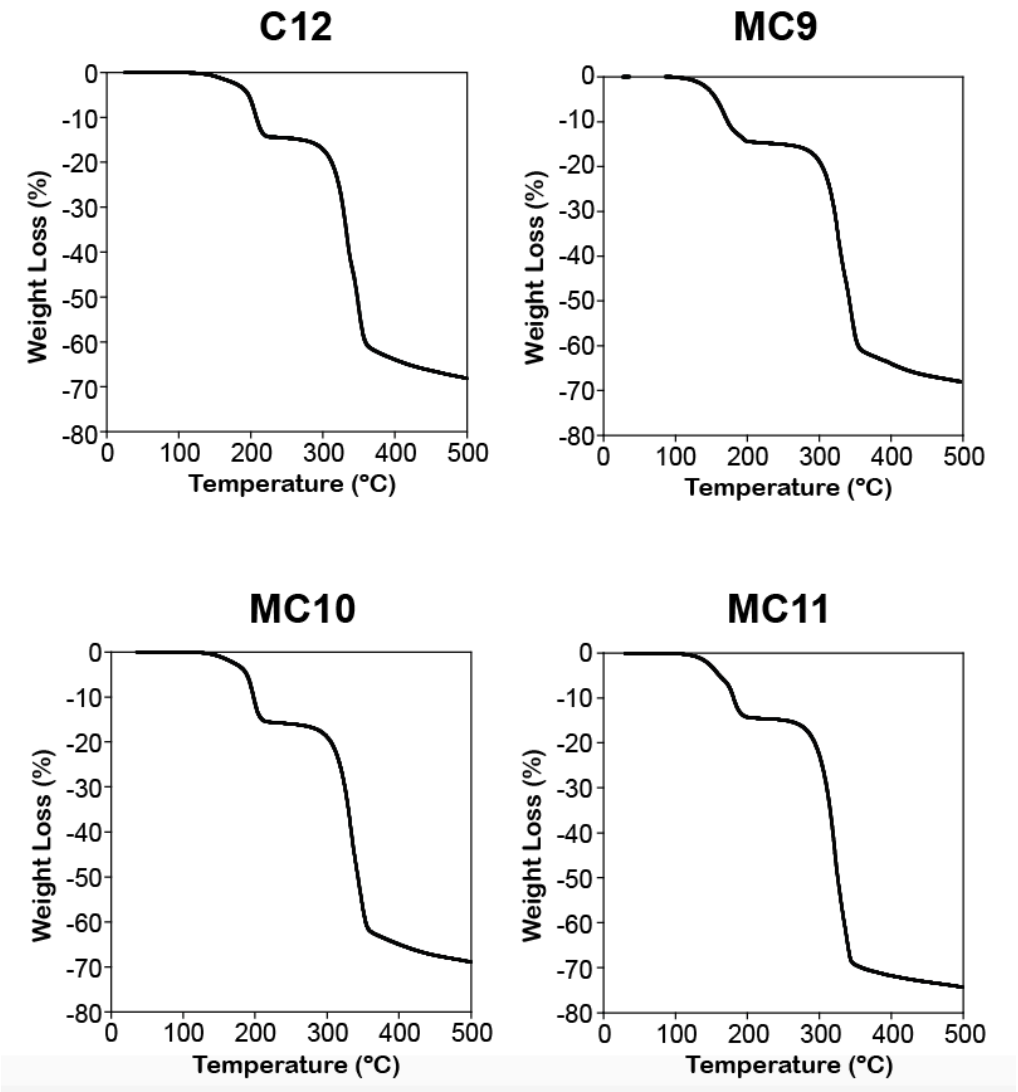


Fig. S12 TGA of **C12** and **MC9**–**MC11**. The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

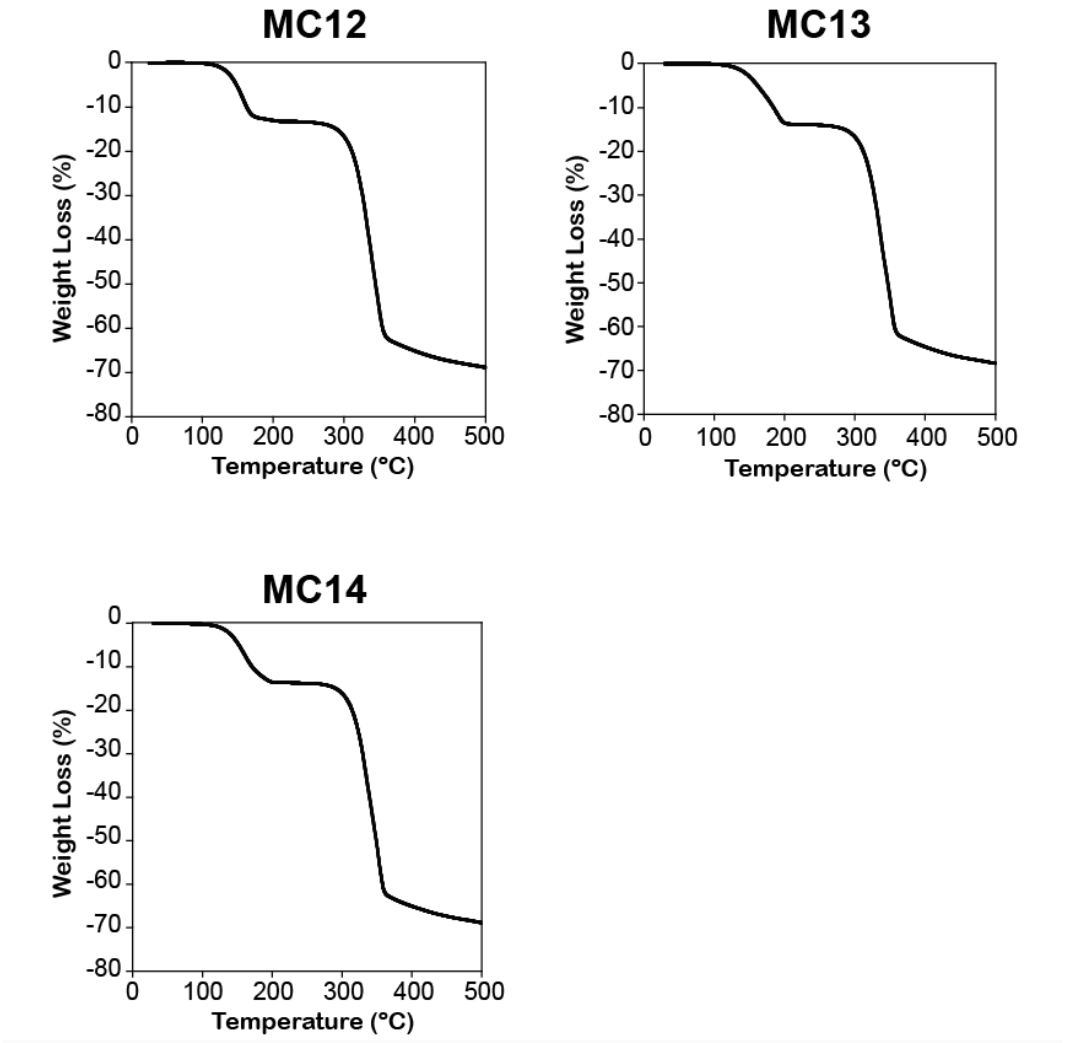


Fig. S13 TGA of **MC12**–**MC14**. The measurements were conducted in nitrogen atmosphere at a heating rate of 10ºC min^{-1}, and the weights of samples were normalized to 100%.

Table S1 Elemental analysis of **C1**-**C14**.

No.	Observed			Calcd [a)]			**NDI/TPFB/Guest**
	C	H	N	C	H	N	
C1	50.47	1.09	3.52	50.60	1.08	3.52	1.0/2.0/1.0
C2	51.90	1.16	3.55	51.71	1.21	3.35	1.0/2.0/2.0
C3	51.87	1.14	3.62	51.71	1.21	3.35	1.0/2.0/2.0
C4	51.87	1.18	3.53	51.71	1.21	3.35	1.0/2.0/2.0
C5	52.85	1.37	3.40	52.84	1.35	3.42	1.0/2.0/2.0
C6	53.13	1.49	3.80	54.03	1.51	3.50	1.0/2.0/2.0
C7	53.11	1.51	3.57	53.33	1.51	3.46	1.0/2.0/2.0
C8	53.39	1.57	3.37	53.33	1.51	3.46	1.0/2.0/2.0
C9	53.15	1.50	3.62	53.33	1.51	3.46	1.0/2.0/2.0
C10	54.70	1.72	3.68	54.57	1.73	3.44	1.0/2.0/2.0
C11	55.48	2.01	3.53	55.33	2.00	3.36	1.0/2.0/2.1
C12	56.44	2.28	3.63	56.09	2.27	3.28	1.0/2.0/2.2
C13	54.17	1.98	3.30	54.06	1.91	3.32	1.0/2.0/2.0
C14	53.24	1.83	3.28	53.05	1.87	3.26	1.0/2.0/2.0

a) The value of C, H, N was calculated as **C1** for **NDI**/**TPFB**/**(trifluoromethyl)benzene** = 1.0/2.0/1.0, **C2** for **NDI**/**TPFB**/***o*-difluorobenzene** = 1.0/2.0/2.0, **C3** for **NDI**/**TPFB**/***m*-difluorobenzene** = 1.0/2.0/2.0, **C4** for **NDI**/**TPFB**/***p*-difluorobenzene** = 1.0/2.0/2.0, **C5** for **NDI**/**TPFB**/**fluorobenzene** = 1.0/2.0/2.0, **C6** for **NDI**/**TPFB**/**benzene** = 1.0/2.0/2.0, **C8** for **NDI**/**TPFB**/***m*-fluorotoluene** = 1.0/2.0/2.0, **C10** for **NDI**/**TPFB**/**toluene** = 1.0/2.0/2.0, **C11** for **NDI**/**TPFB**/***m*-xylene** = 1.0/2.0/2.1 and **C12** for **NDI**/**TPFB**/**mesitylene** = 1.0/2.0/2.2, **C13** for **NDI**/**TPFB**/***m*-methylanisole** = 1.0/2.0/2.0, **C14** for **NDI**/**TPFB**/**1,3-dimethoxybenzene** = 1.0/2.0/2.0

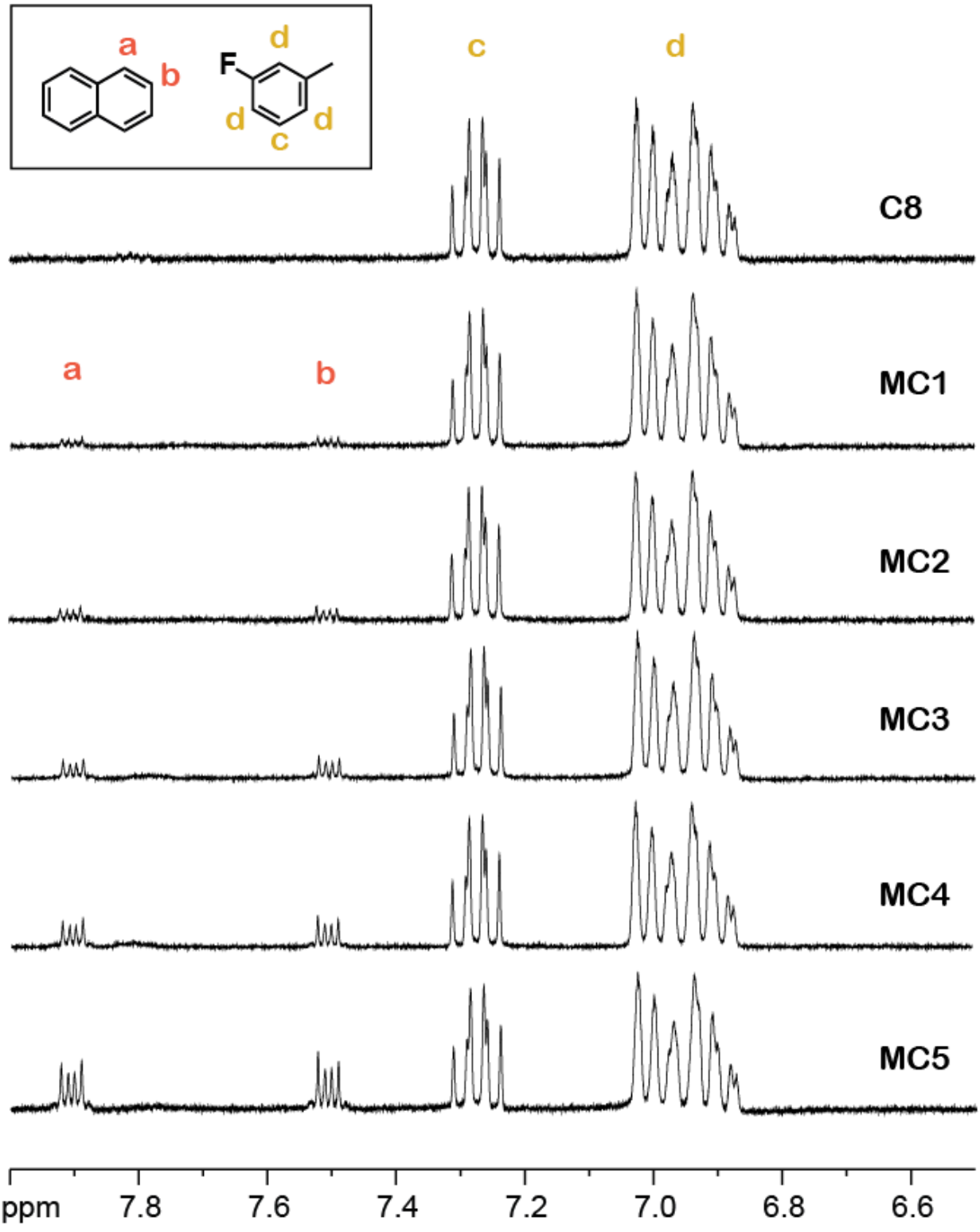


Fig. S14 ^{1}H NMR spectra of the **C8** and **MC1–MC5** dissolved in acetone-d_6.

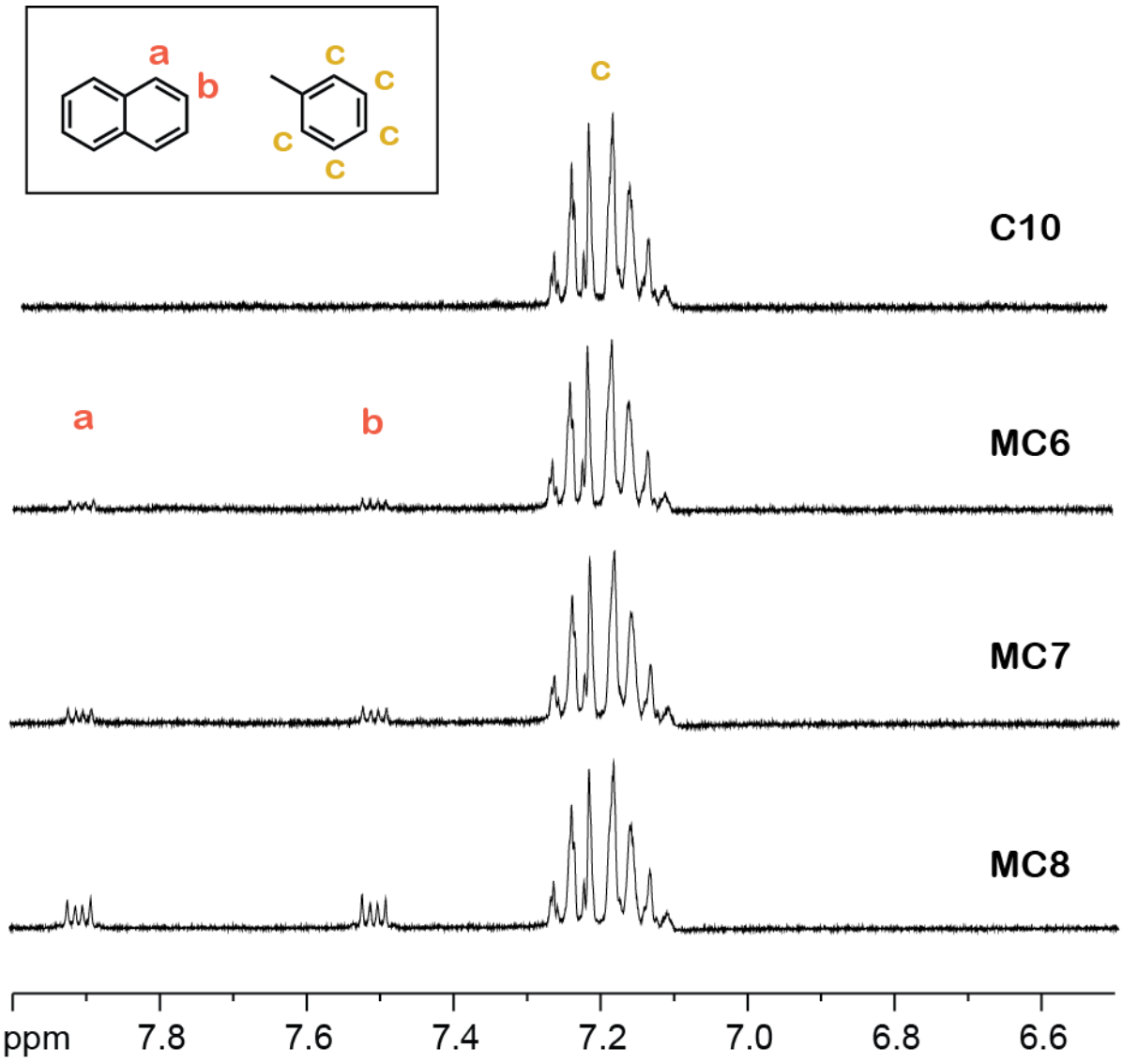


Fig. S15 ^{1}H NMR spectra of the **C10** and **MC6–MC8** dissolved in acetone-d_6.

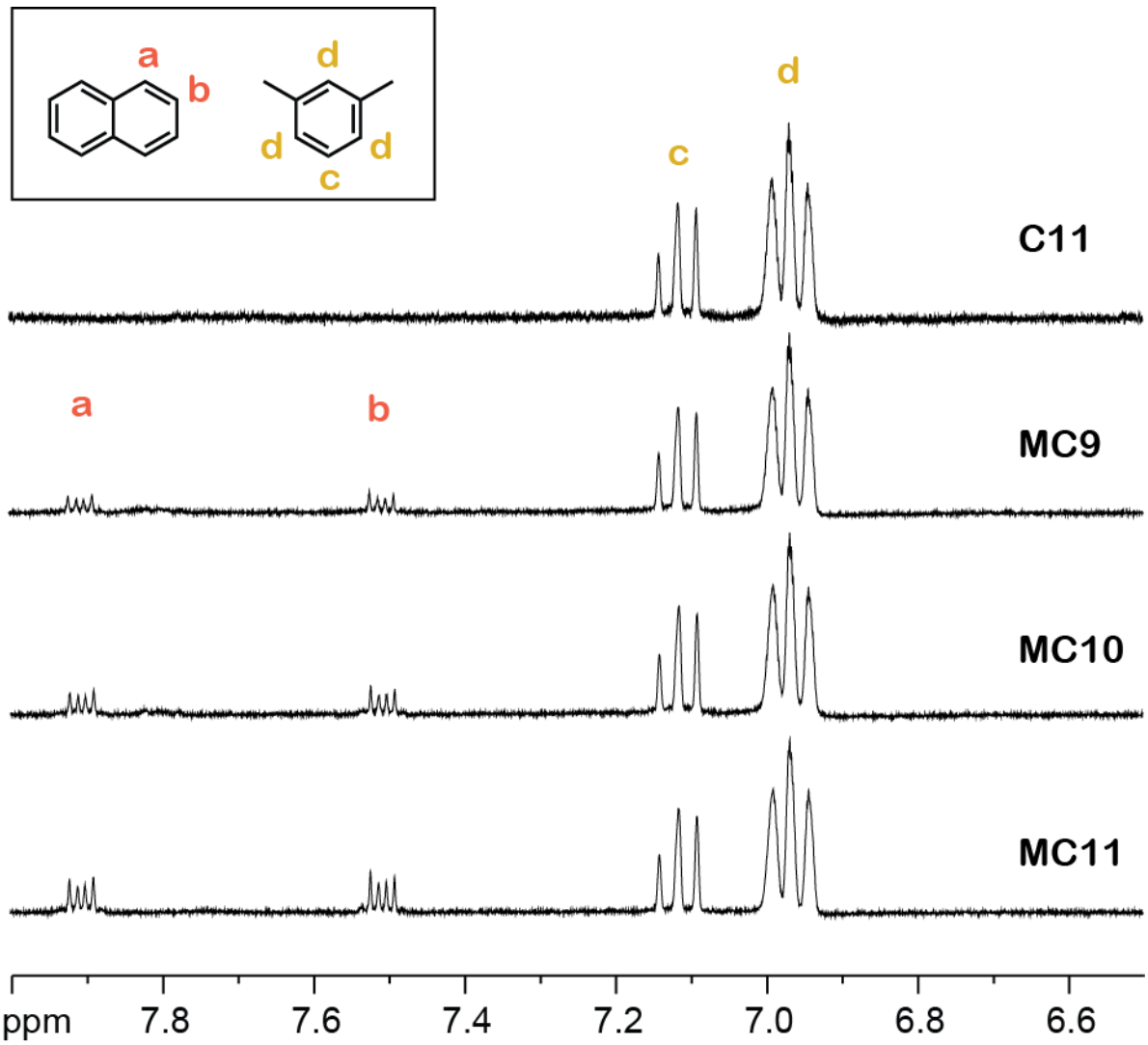


Fig. S16 ^{1}H NMR spectra of the **C11** and **MC9–MC11** dissolved in acetone-d_6.

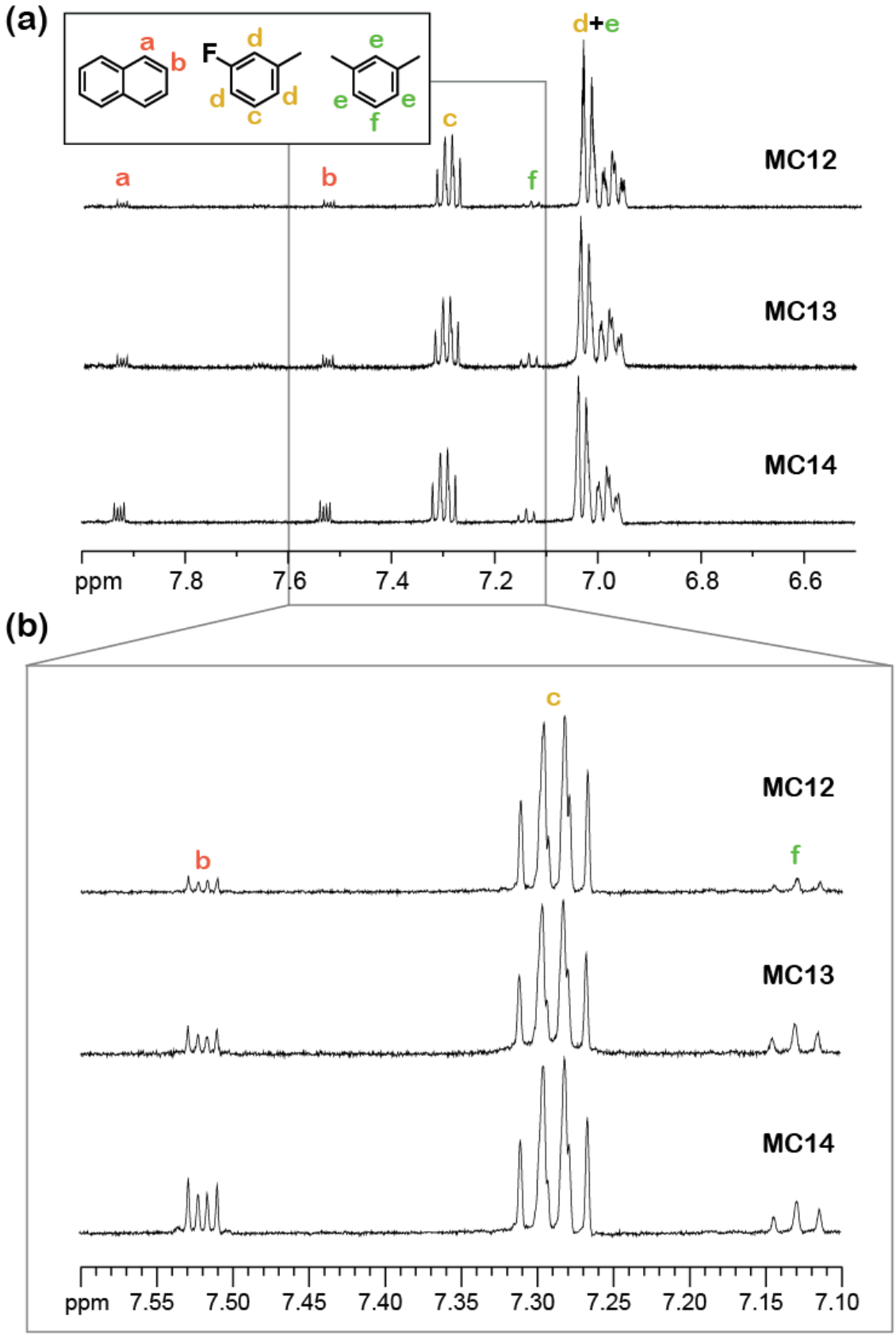


Fig. S17 ^{1}H NMR spectra of the **MC12–MC14** dissolved in DMSO-d_6.

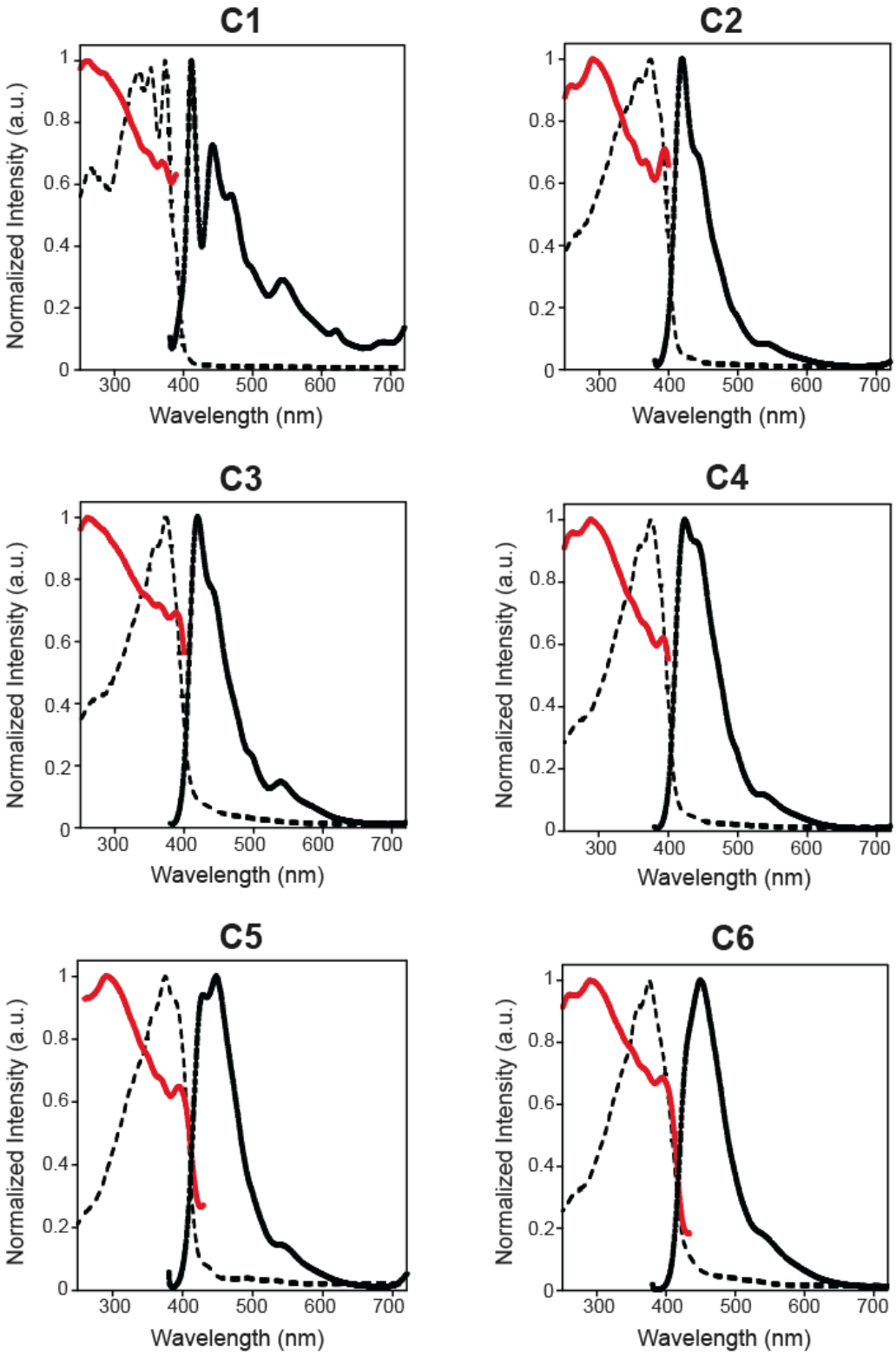


Fig. S18 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **C1–C6**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.

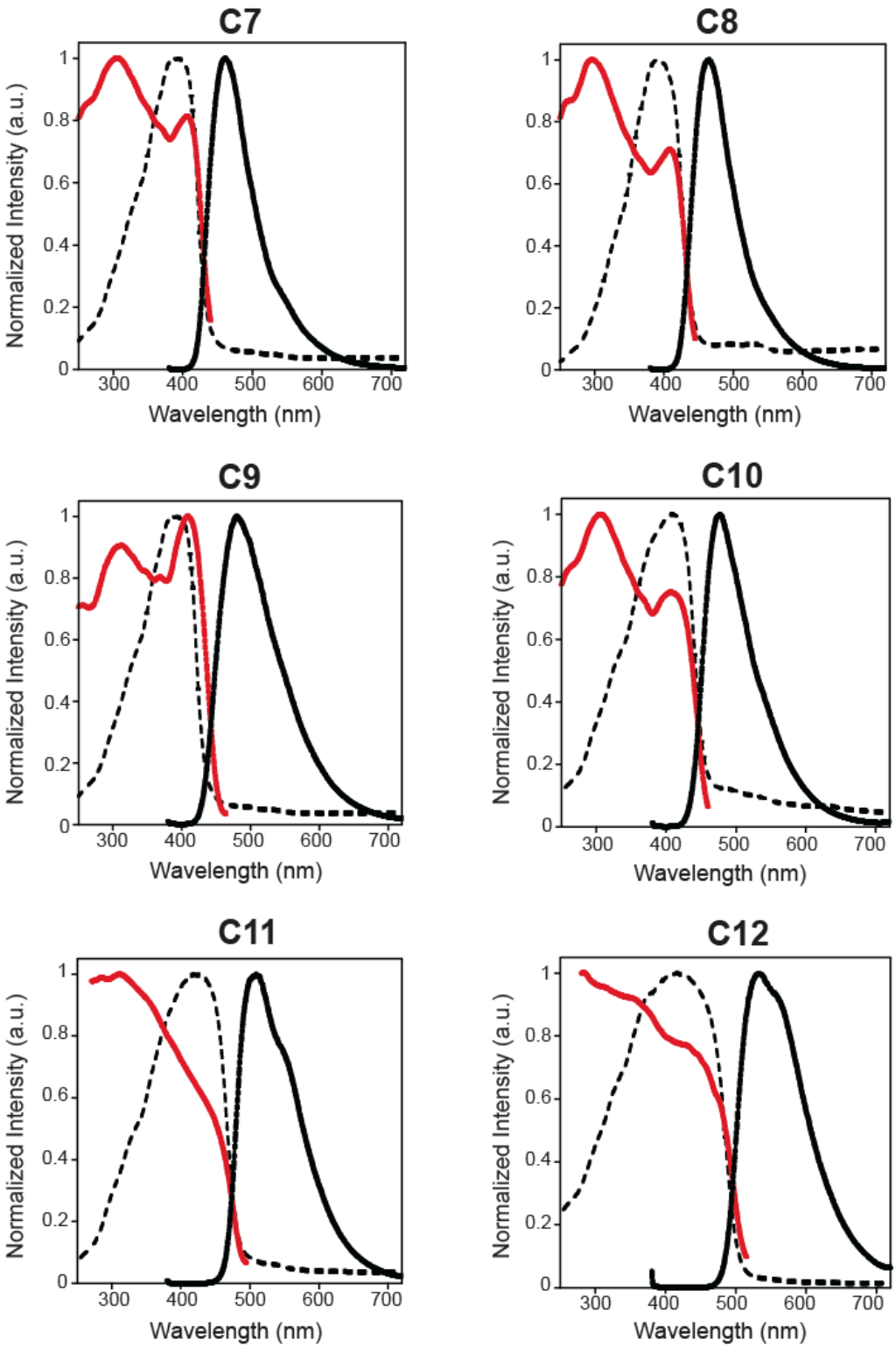


Fig. S19 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **C7–C12**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.

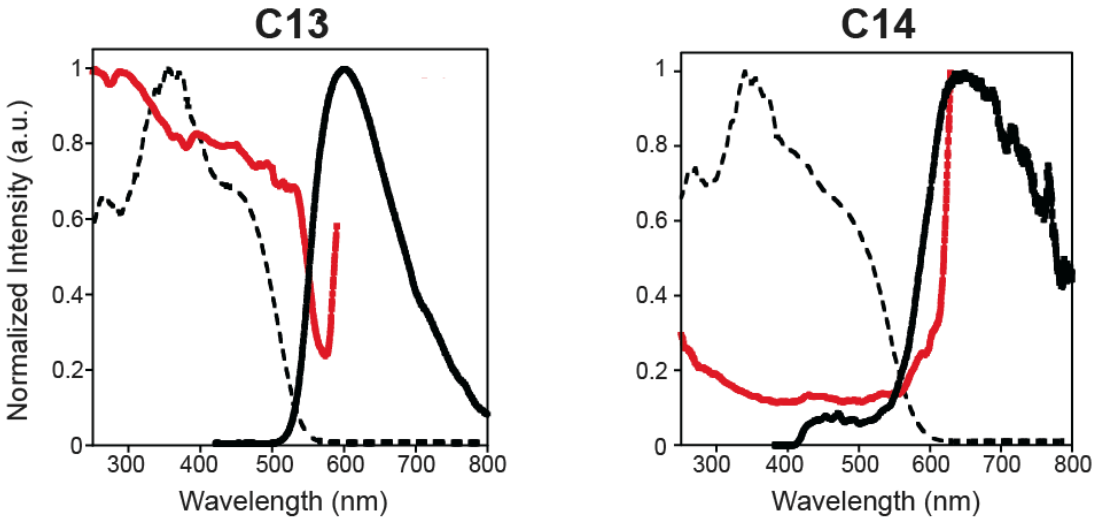


Fig. S20 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **C13–C14**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.

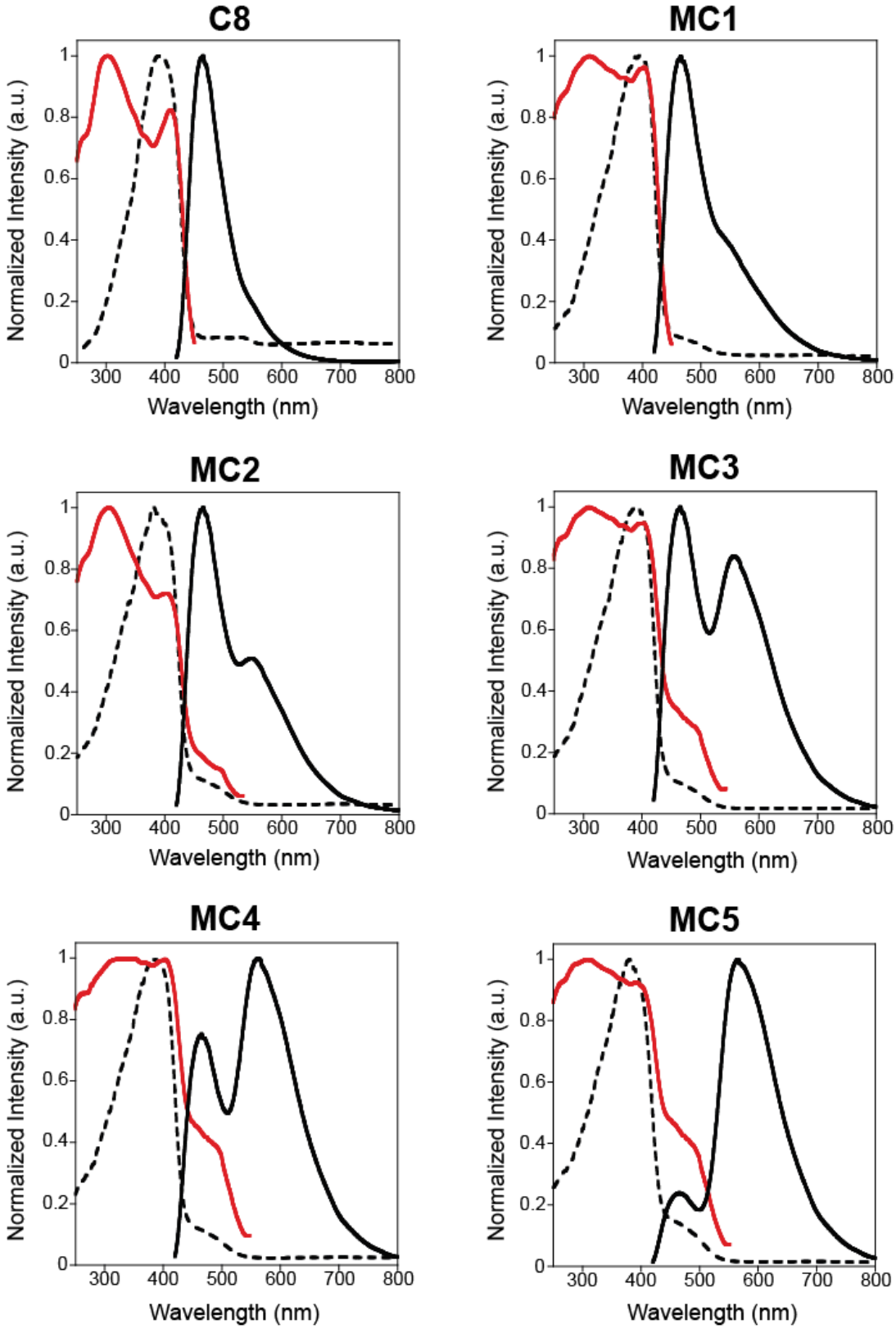


Fig. S21 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **C8** and **MC1–MC5**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.

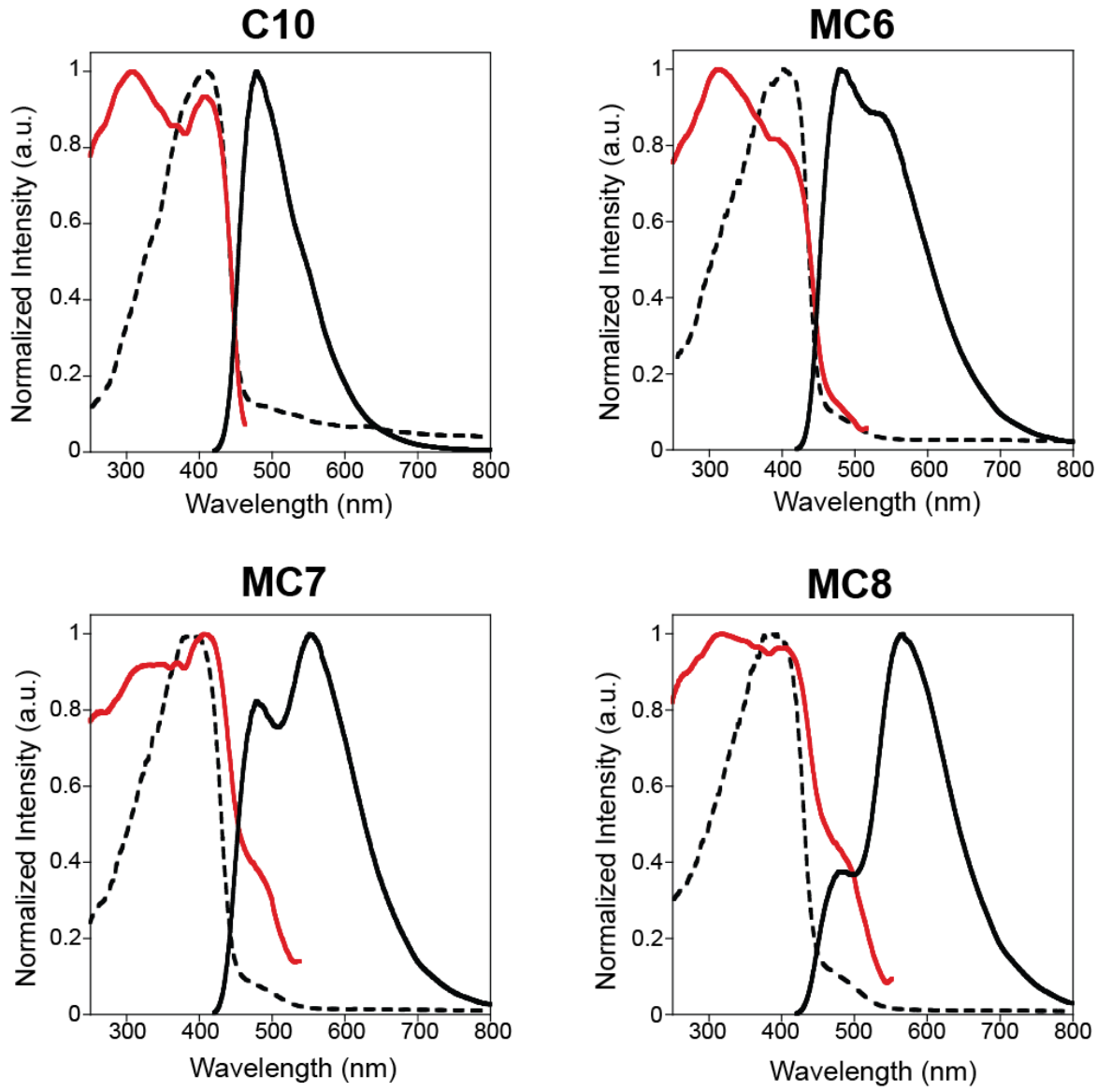


Fig. S22 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **C10** and **MC6**–**MC8**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.

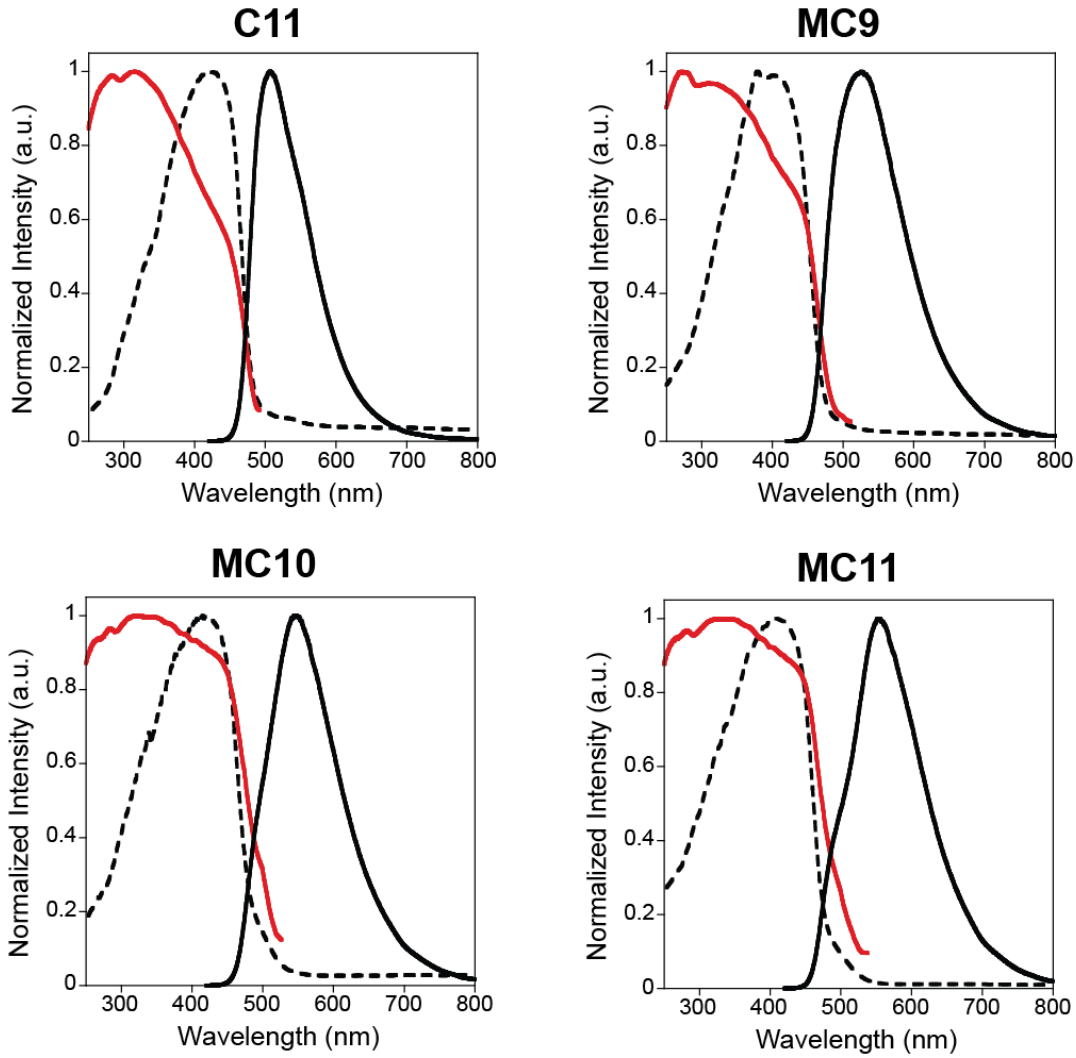


Fig. S23 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **C12** and **MC9**–**MC11**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.

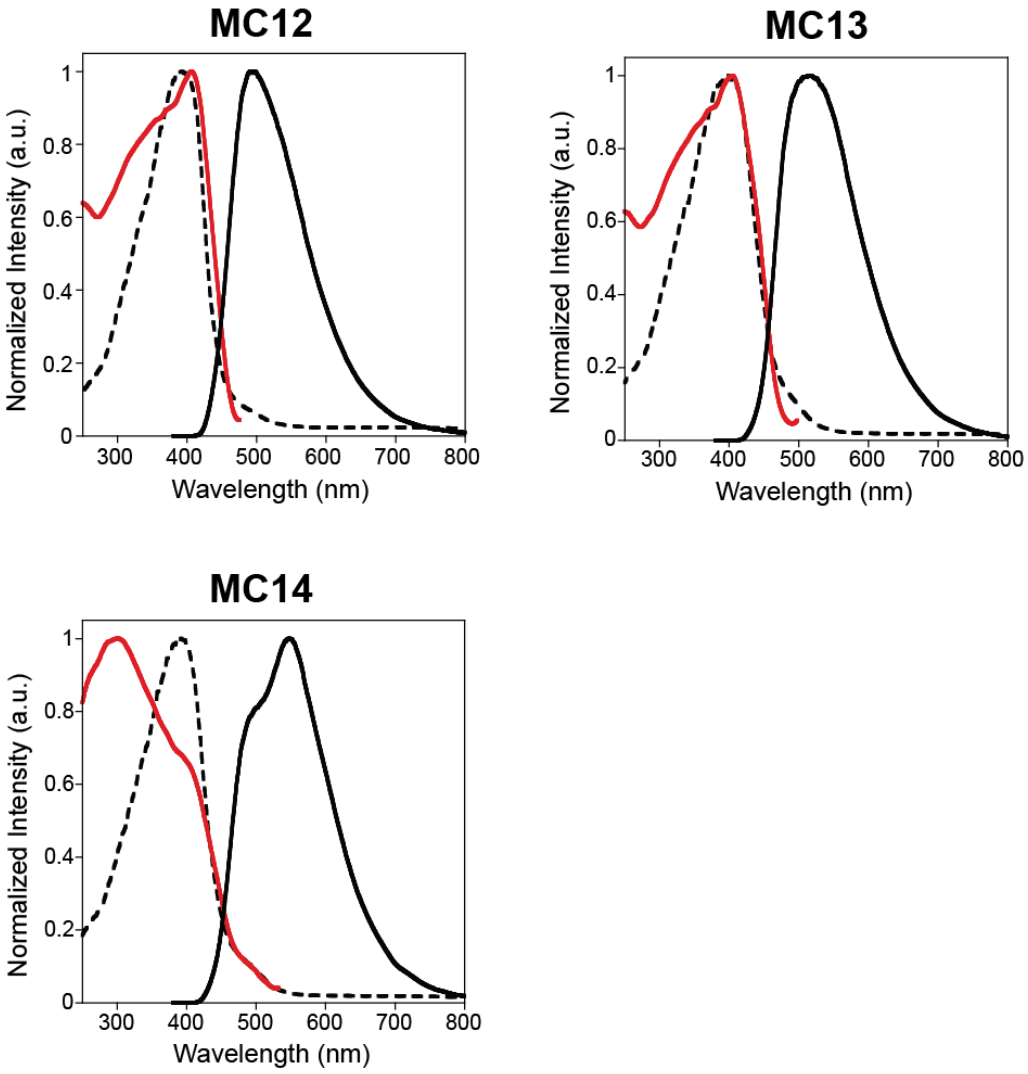


Fig. S24 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **MC12**–**MC14**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.

Lifetime Measurements

The following multi exponential emission decay model is applied to fit the whole image:

$$I_r(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) + A_4 \exp\left(-\frac{t}{\tau_4}\right) +$$

Where $I_r(t)$ is the emission counts that were collected at time t after excitation. A_1, A_2, A_3, and A_4 are the preexponential factors related with the statistical weights of each exponential and τ_1, τ_2, τ_3, and τ_4 are the lifetimes from the short and long components respectively (summarized in Table S2). The quality of the nonlinear curve fit was determined and statistically measured by the minimum reduced chi-squared (χ^2). A perfect fit would have the value of 1.0.

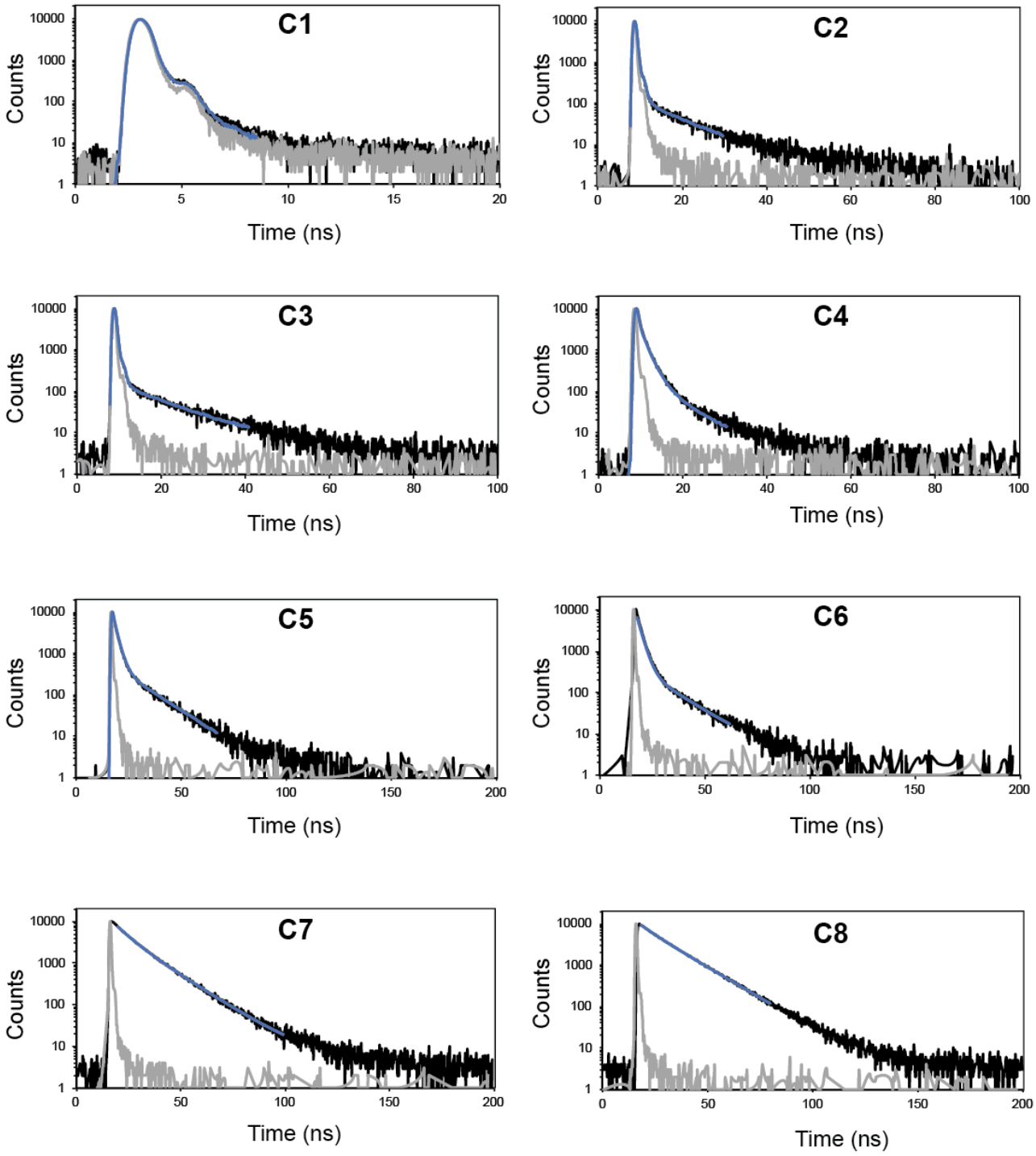


Fig. S25 Emission decay curves (black line), fits (blue line), and instrument response function (IRF) (gray line) of **C1–C8**. Excitation at 365 nm.

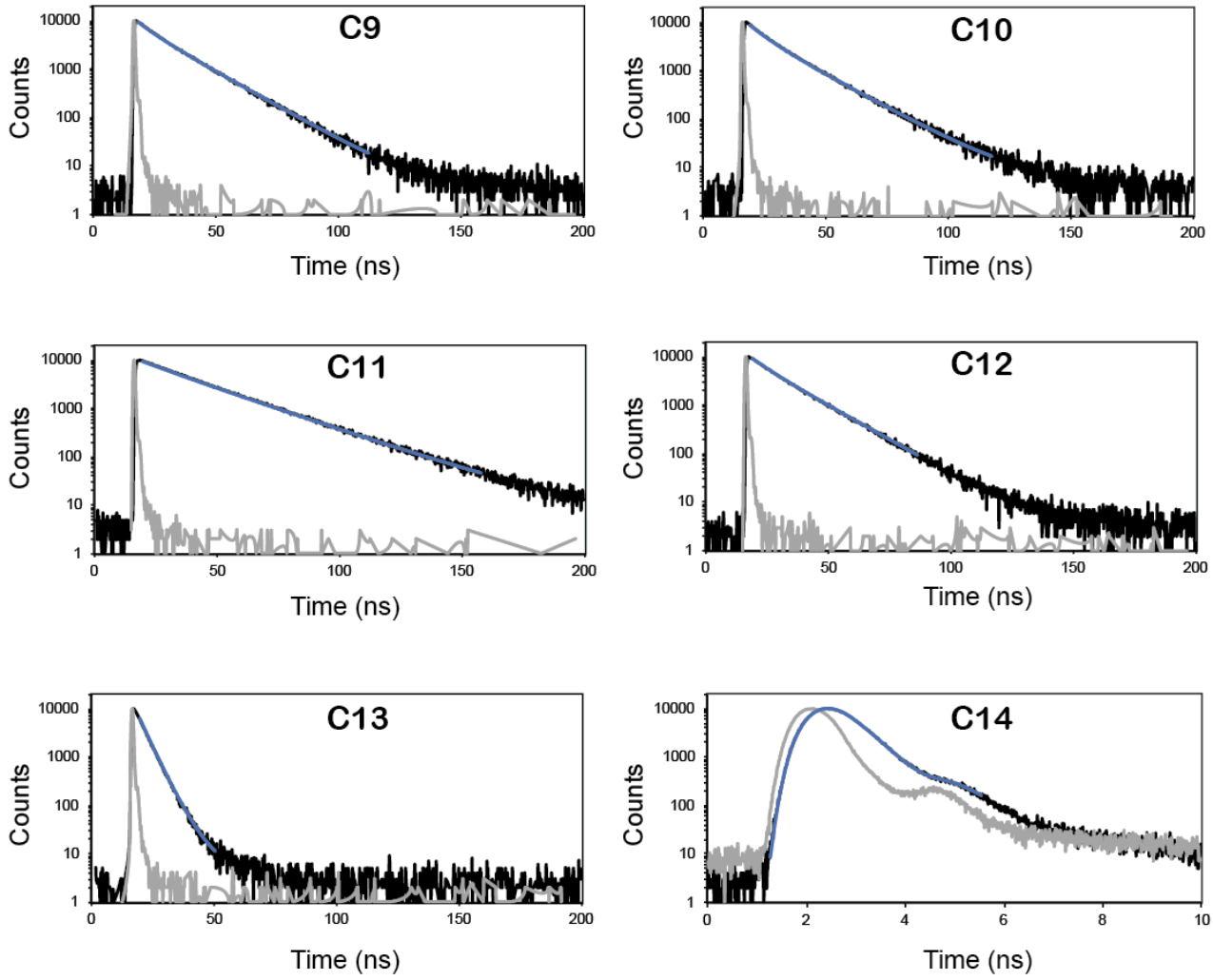


Fig. S26 Emission decay curves (black line), fits (blue line), and instrument response function (IRF) (gray line) of **C9–C14**. Excitation at 365 nm.

Table S2 Summary of lifetime analyses for **C1–C14**. Emission lifetimes (τ), preexponetial factor in percentage (% A). λ = emission wavelength of registration after excitation at 365 nm and τ_{av} intensity average lifetime.

No.	Guest	λ/nm	CHI	τ_{av}/ns	τ_1/ns	τ_2/ns	τ_3/ns	A_1	A_2	A_3
C1	(trifluoromethyl)benzene	412	1.35	0.1	0.06	0.1	-	3249	9	-
C2	*o*-difluorobenzene	420	1.23	1.3	0.2	0.1	10.8	4466	77	11
C3	*m*-difluorobenzene	420	1.10	1.6	0.2	0.7	11.1	4751	245	14
C4	*p*-difluorobenzene	420	1.31	1.6	0.4	1.7	6.9	2373	472	24
C5	fluorobenzene	448	1.29	4.1	0.6	1.9	13.0	1605	1883	95
C6	benzene	450	1.18	4.9	2.3	13.2	-	7387	397	-
C7	*o*-fluorotoluene	460	1.10	11.9	6.4	13.8	-	3430	4643	-
C8	*m*-fluorotoluene	466	0.96	14.0	6.2	14.7	-	1677	7785	-
C9	*p*-fluorotoluene	480	1.05	14.1	6.1	15.2	-	2404	7149	-
C10	toluene	472	1.07	14.1	6.5	15.9	-	3173	5743	-
C11	*m*-xylene	509	1.09	24.9	15.1	26.4	-	1954	7790	-
C12	mesitylene	531	1.11	14.6	7.1	15.6	-	2222	7166	-
C13	*m*-methylanisole	600	1.02	4.2	3.8	6.8	-	6450	517	-
C14	1,3-dimethoxybenzene	640	1.18	0.4	0.1	0.4	-	-181	376	-

Reference sample (MC15–MC17)

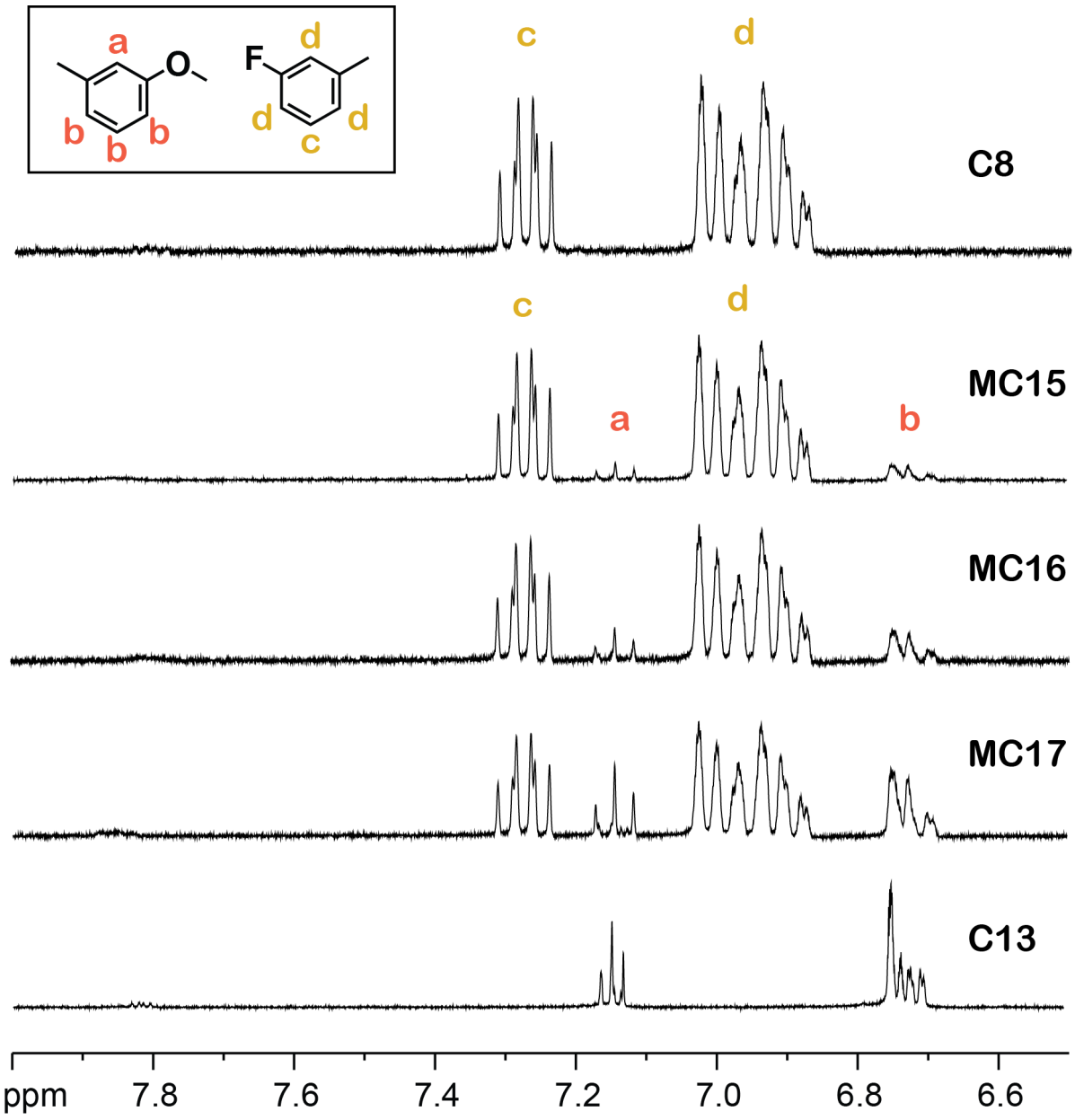


Fig. S27 ^{1}H NMR spectra of the **C8**, **MC15–MC17**, and **C13** dissolved in acetone-d_6.

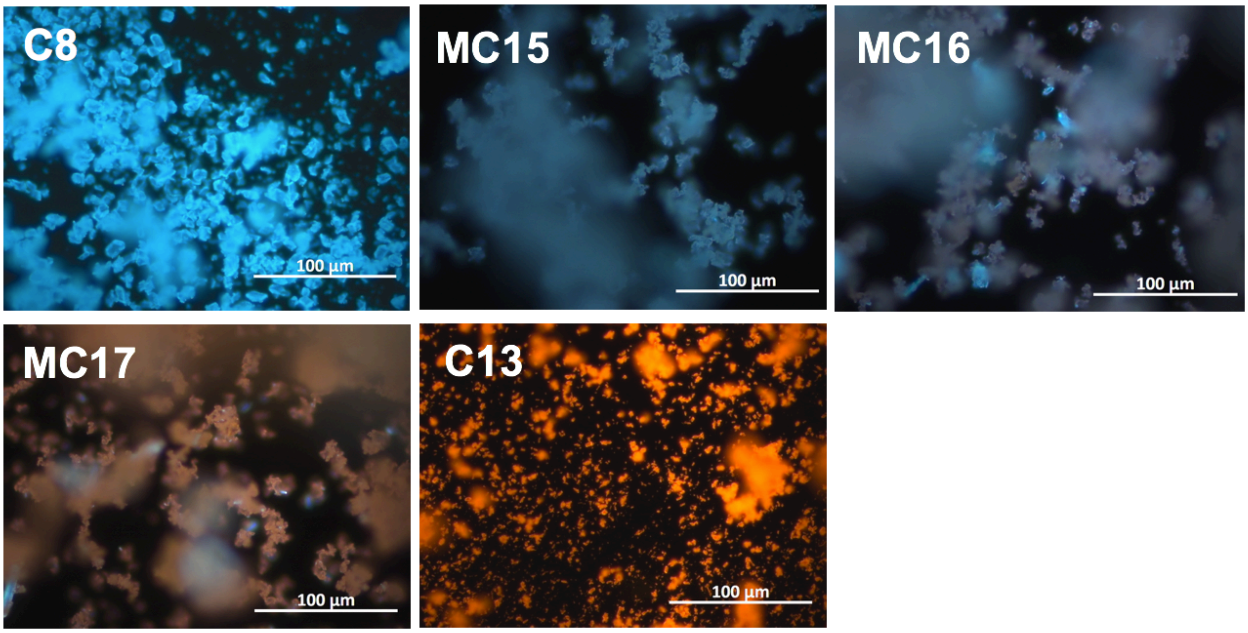


Fig. S28 Photograph of **C8**, **MC15–MC17** and **C13** crystals under fluorescence microscope. Scale bar = 100µm, Excitation = 330-380 nm, Emission > 420 nm.

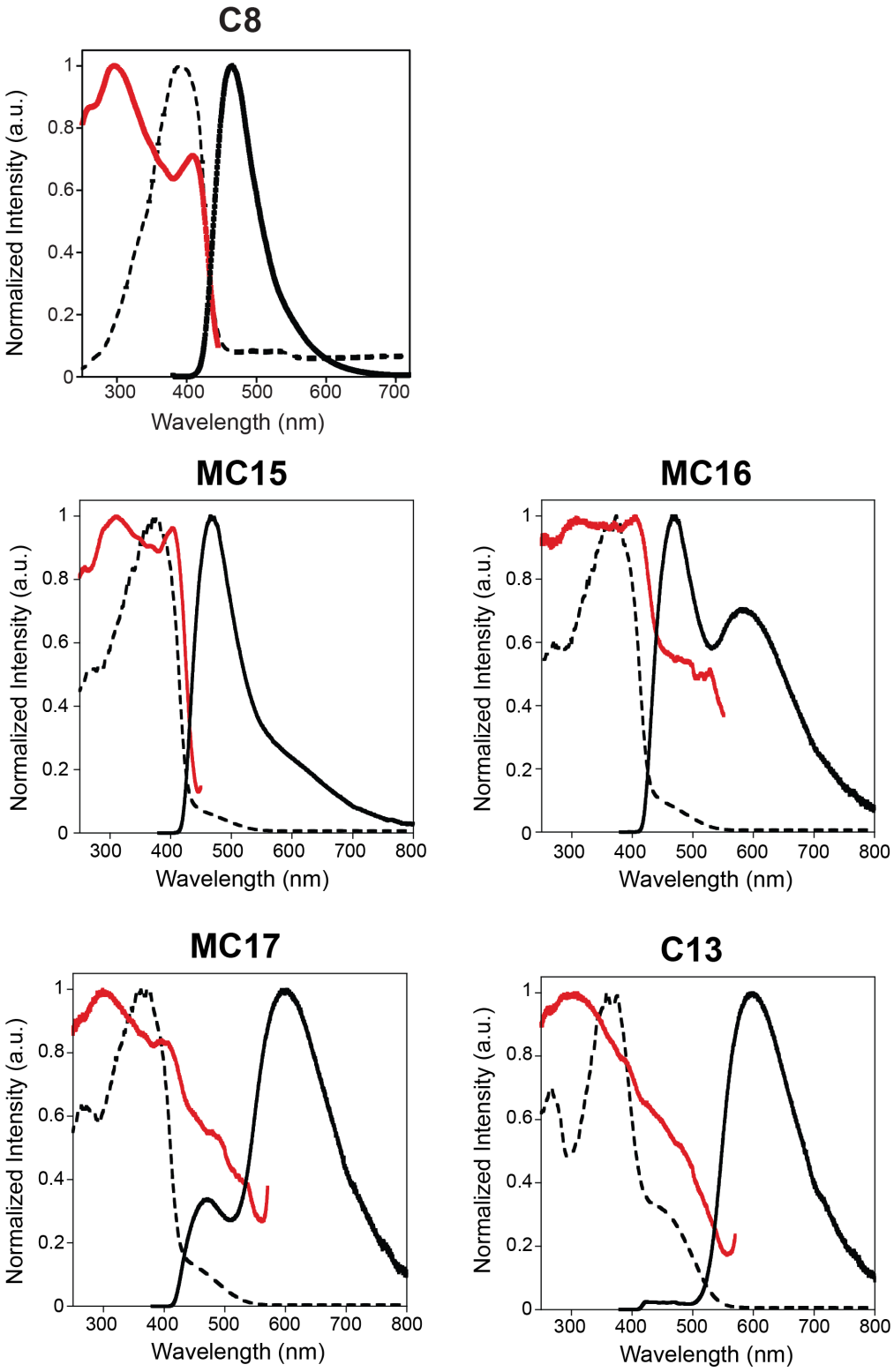


Fig. S29 Emission (solid line), excitation (dashed line), and diffuse reflection spectra (solid red line) of **C8**, **MC15**–**MC17** and **C13**. Emission spectra were obtained under excitation at 370 nm. Excitation spectra were obtained at their emission peak.