Structural Study of Three Isomers of Tm@C_{82} by ^{13}C-NMR Spectroscopy.

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Supporting Information

(experimental details)

[HPLC chromatograms]

Figure 1a shows the HPLC chromatogram of the first stage (a Buckyprep column 20mm × 250mm; toluene; flow rate 12ml/min). Tm@C_{82} was found in the tail of a hollow C_{84} fraction indicated in the figure. Figure 1b shows the HPLC chromatogram of the second stage (two Buckyprep column 20mm × 250mm; toluene; flow rate 12ml/min). Tm@C_{82}(I) was separated from the other two isomers. Figure 1c shows the HPLC chromatogram of the third stage for Tm@C_{82}(I) (two Buckyprep column 20mm × 250mm; toluene; flow rate 12ml/min). Figure 1d shows the HPLC chromatogram of the fourth stage for Tm@C_{82}(I) (a 5PBB column 20mm × 250mm; toluene; flow rate 12ml/min). Empty fullerenes were removed and Tm@C_{82}(I) was isolated. Figure 1e shows the HPLC chromatogram of the third stage of Tm@C_{82}(II) and Tm@C_{82}(III) (two Buckyprep column 20mm × 250mm; toluene; flow rate 12ml/min). They were roughly separated from each other and the empty fullerenes were removed. Figure 1f shows the HPLC chromatogram of the fourth stage for Tm@C_{82}(II) and Tm@C_{82}(III) (a Buckyclutcher column 20mm × 250mm; toluene; flow rate 12ml/min). Tm@C_{82}(II) and Tm@C_{82}(III) were completely isolated each other.

[^{13}C-NMR spectra of Tm@C_{82}(II) in a proton-coupled mode and in a proton-decoupled mode]

Figure S2 shows the ^{13}C-NMR spectra of Tm@C_{82}(II) in CS_2 solution at room temperature; (a) and (b) were measured in a mode and a proton-decoupled mode respectively.

[Temperature dependent ^{13}C-NMR spectra of Tm@C_{82}(II)]

Figure S3 shows the temperature dependent ^{13}C-NMR spectra of Tm@C_{82}(II) in CS_2 solution; (a), (b), and (c) were measured at 0°C, 22°C, and 35°C respectively.

[Absorption spectra of three isomers of Tm@C_{82}]

Each isomer was identified with those reported by Dunsch et al. by comparing the absorption spectra. Figure S4 shows the absorption spectra of Tm@C_{82}(I), Tm@C_{82}(II), and Tm@C_{82}(III) in CS_2 solution at room temperature.

[ESR spectra of three isomers of Tm@C_{82}]

Figure S5 shows the ESR spectra of Tm@C_{82}(I), Tm@C_{82}(II), and Tm@C_{82}(III) in CS_2 solution at 5K. The peaks marked with a solid square were assigned to paramagnetic impurities. The broad feature marked with an open square in the spectrum of isomer II was due to baseline instability. Detailed analysis is now in progress.

[Line positions and relative intensities in the ^{13}C-NMR spectra of three isomers of Tm@C_{82}]

Table S1 shows the line positions and relative intensities in the ^{13}C-NMR spectra of three isomers of Tm@C_{82} at room temperature.

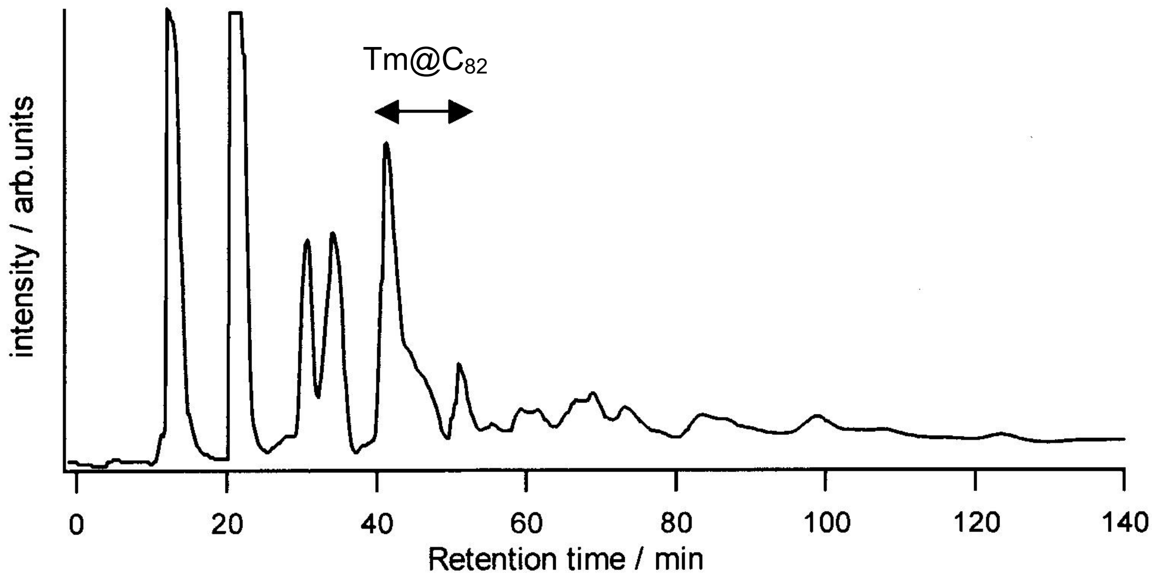


Figure S1a

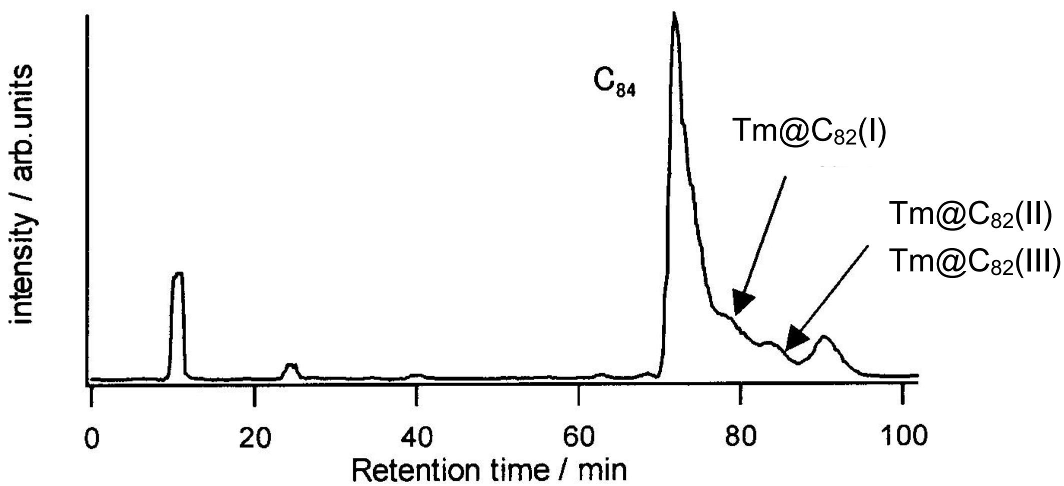


Figure S1b

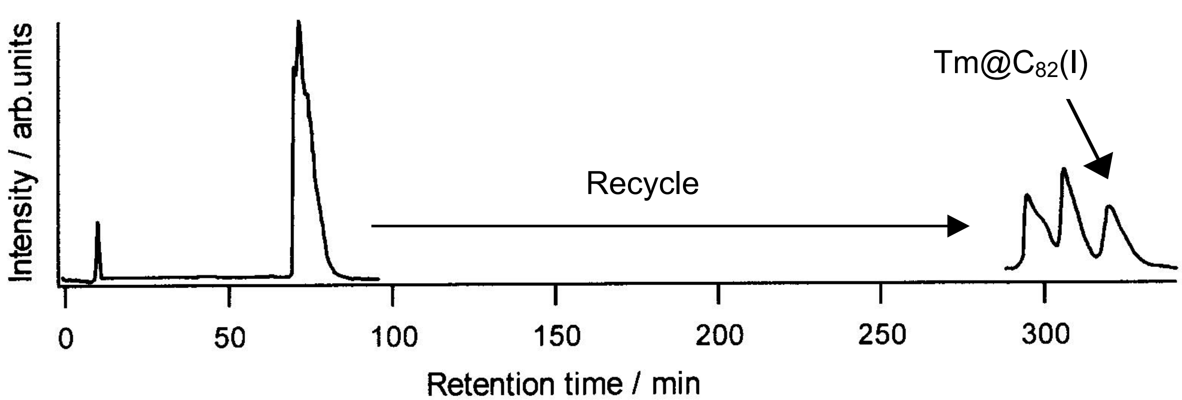


Figure S1c

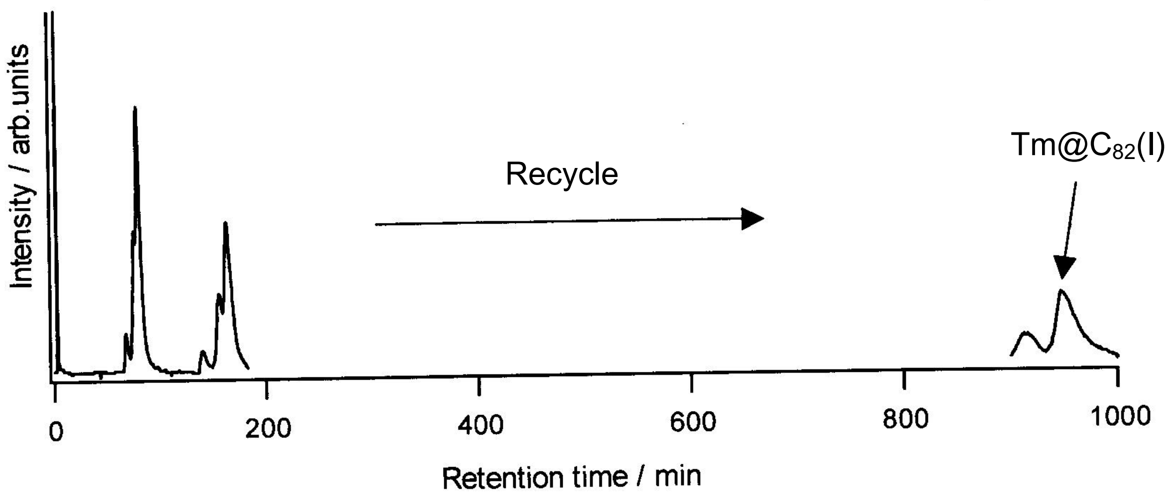


Figure S1d

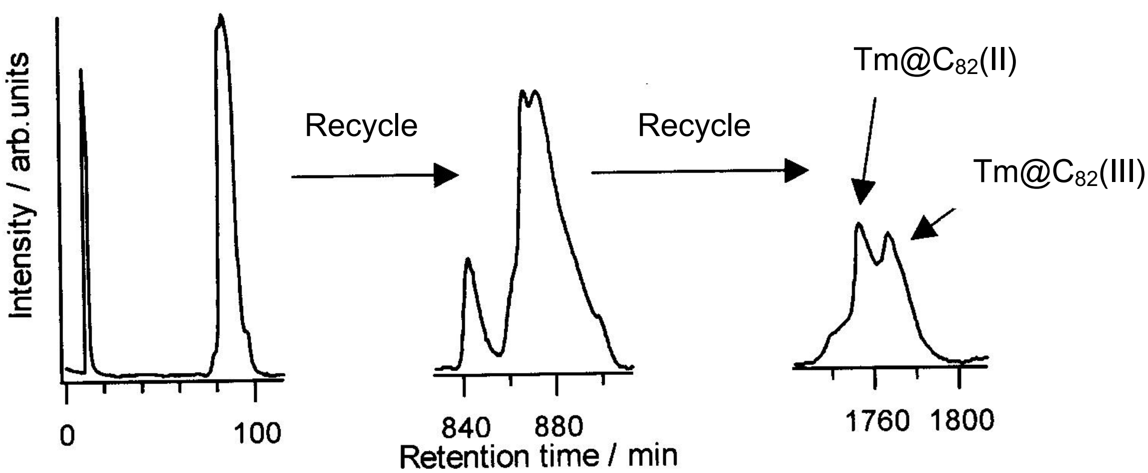


Figure S1e

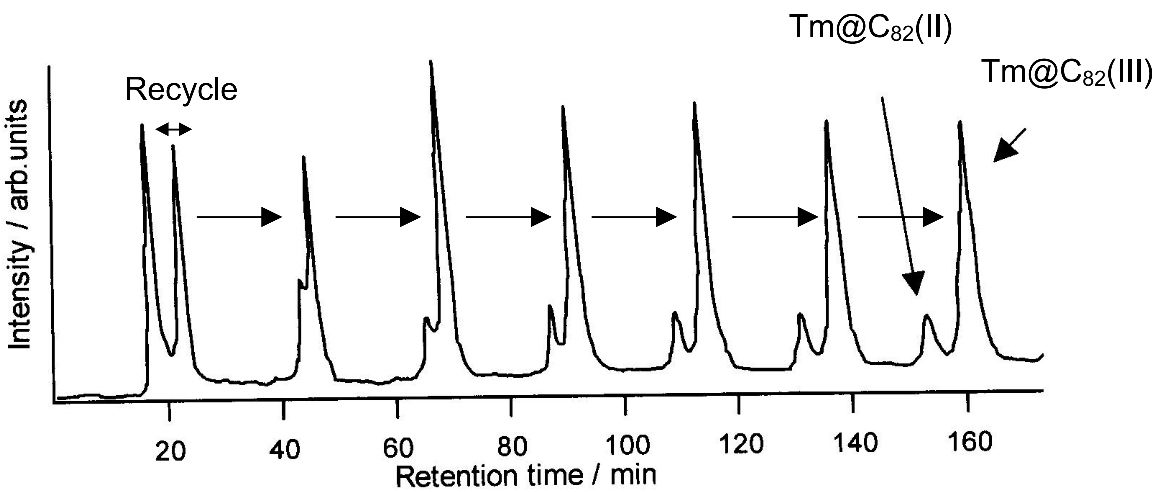


Figure S1f

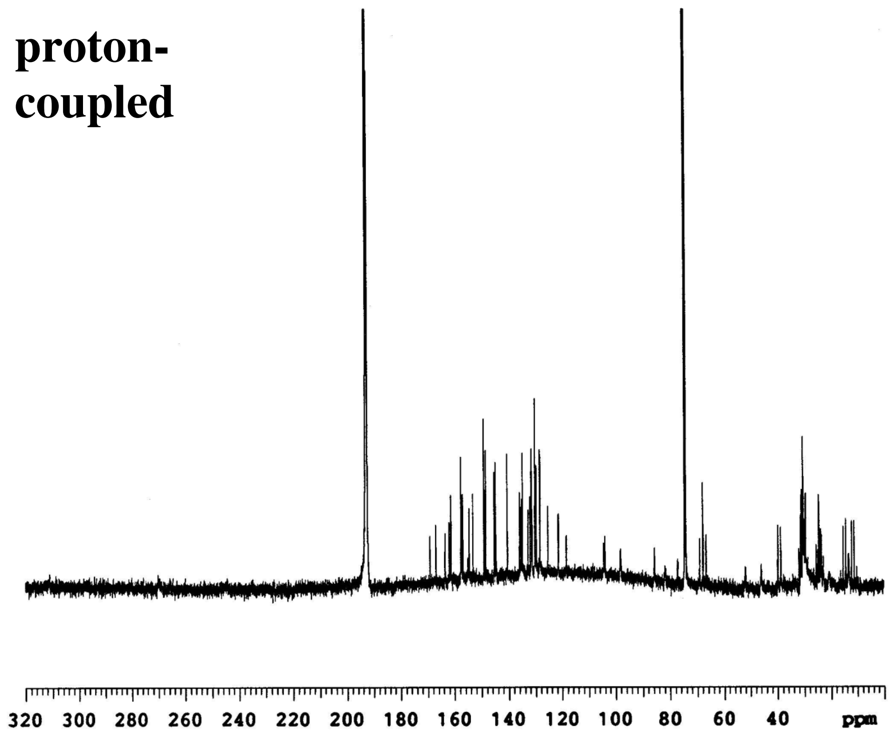


Figure S2a

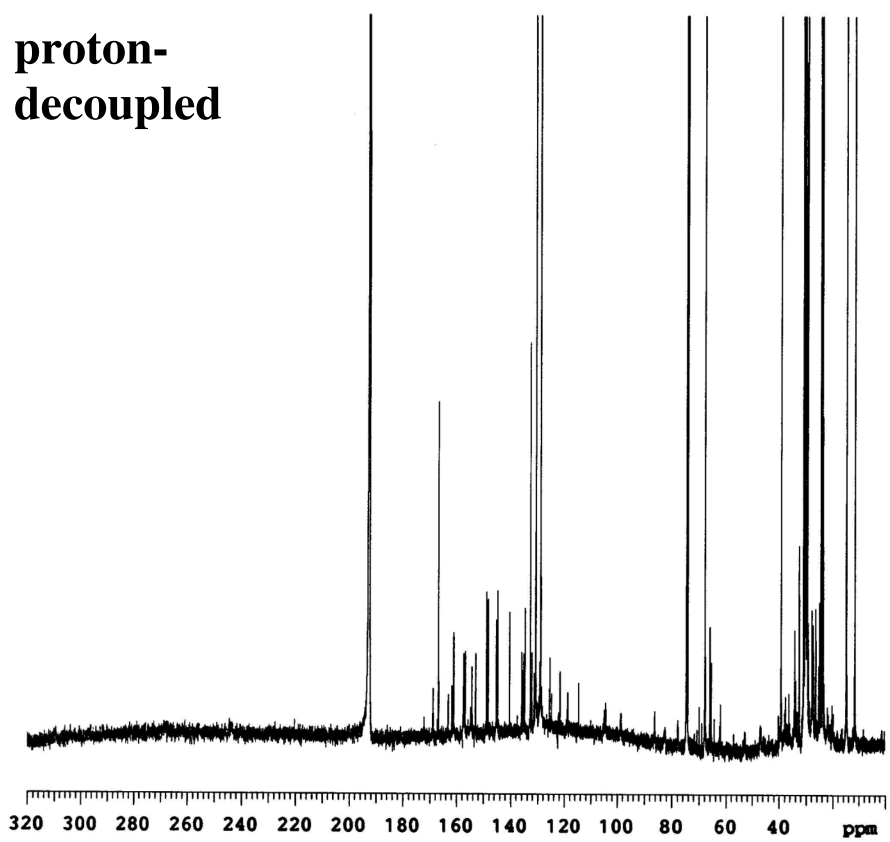


Figure S2b

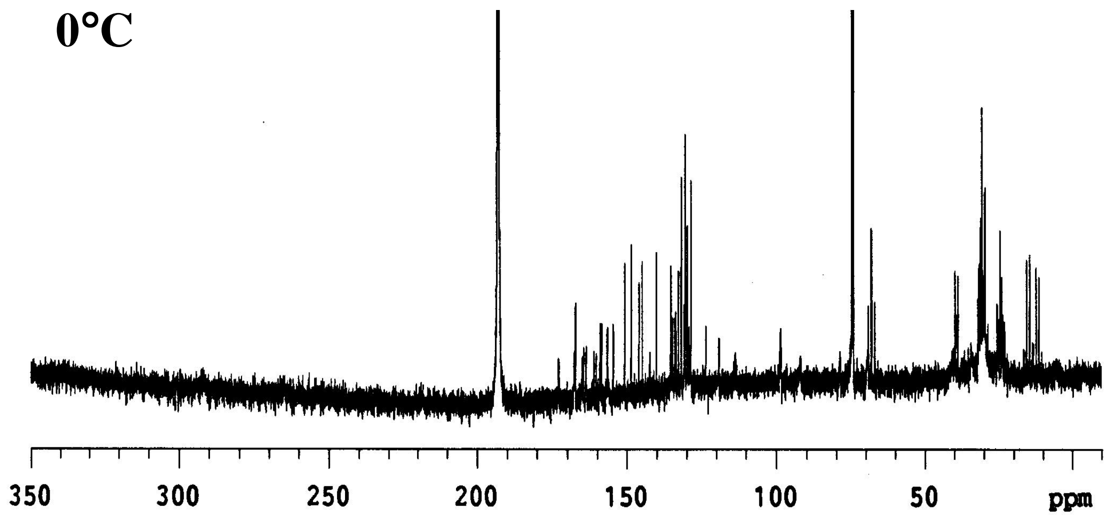


Figure S3a

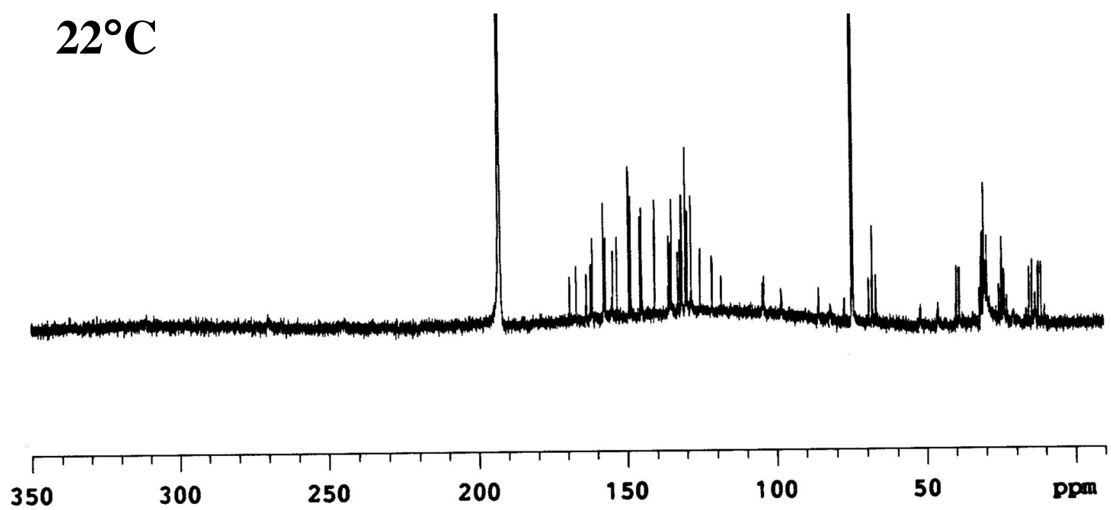


Figure S3b

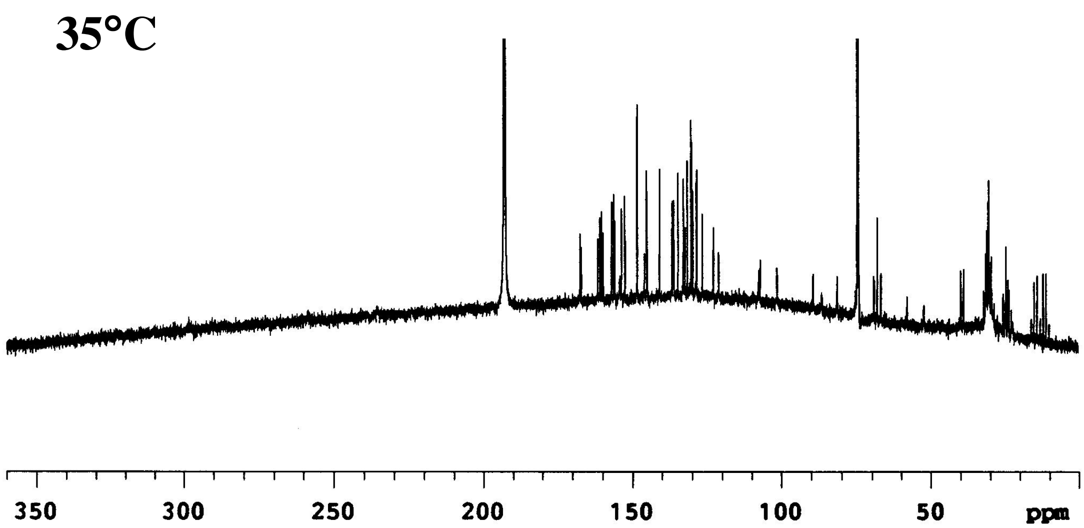
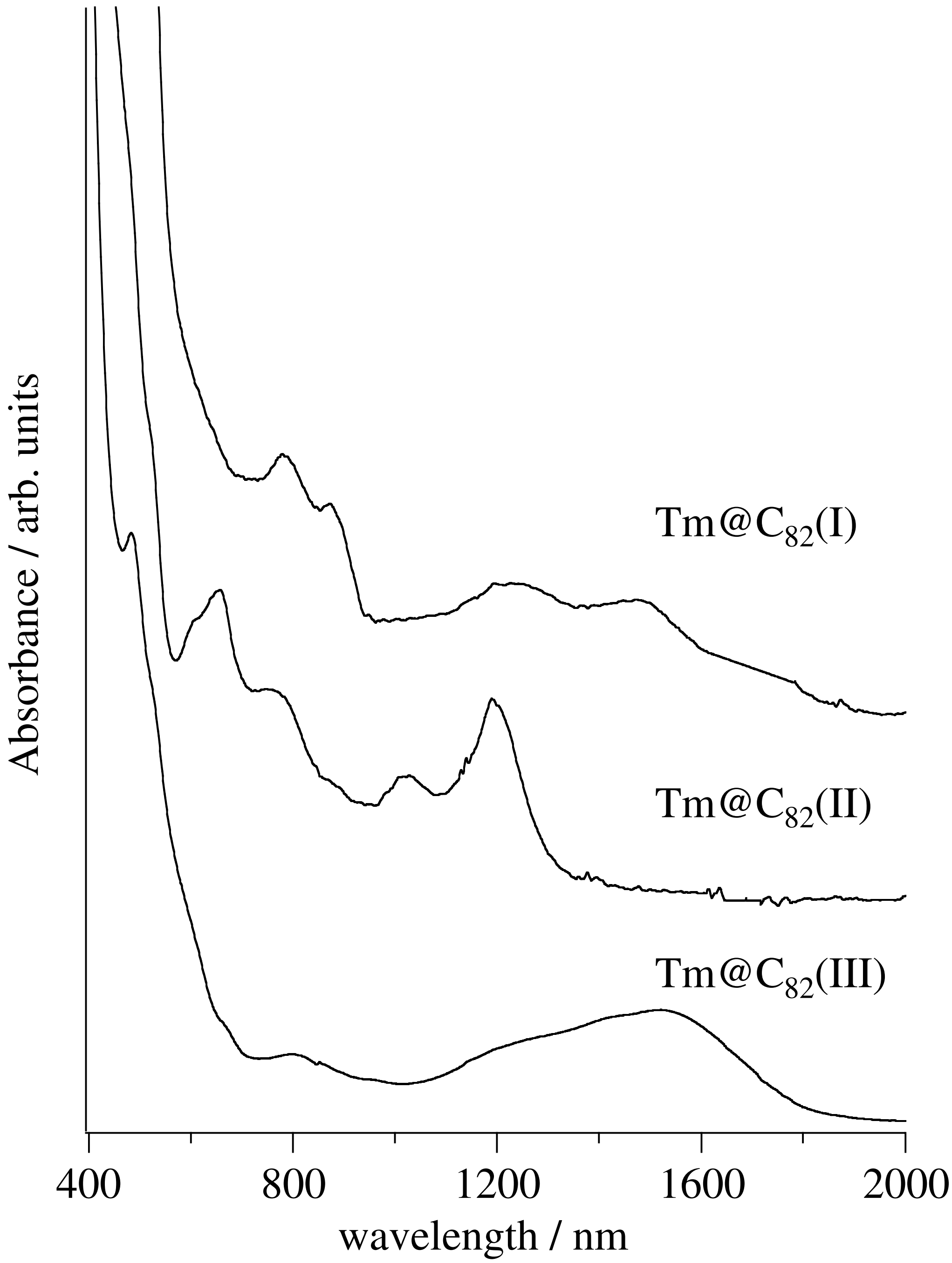


Figure S3c



Absorbance / arb. units
Tm@C82(I)
Tm@C82(II)
Tm@C82(III)
400
800
1200
1600
2000
wavelength / nm

Figure S4

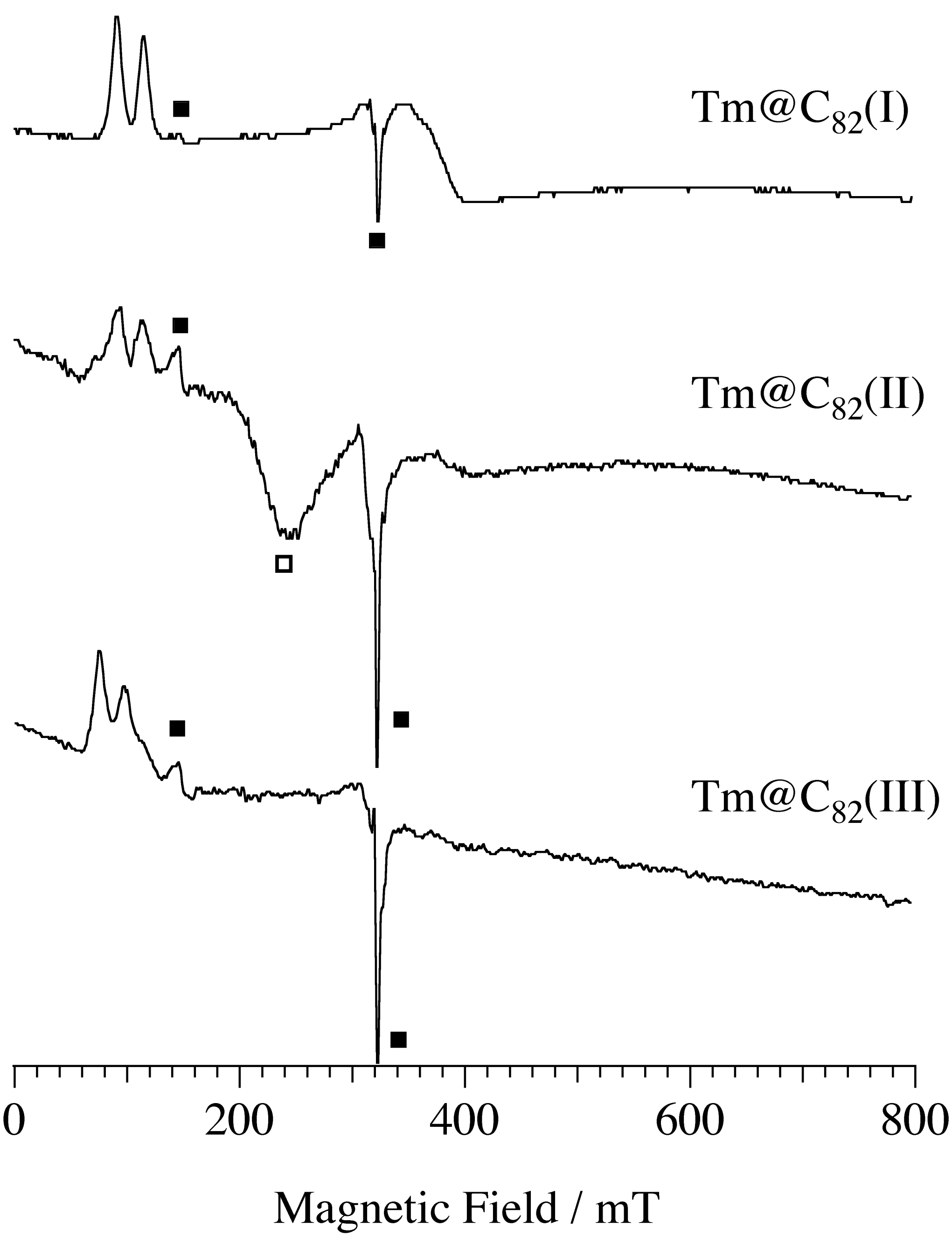


Figure S5

Table S1 Line positions and relative intensities in the ^{13}C-NMR spectra of three isomers of $Tm@C_{82}$ at room temperature.

	Isomer I		Isomer II		Isomer III	
No.	Shift (ppm)	Relative intensity	Shift (ppm)	Relative intensity	Shift (ppm)	Relative intensity
1	48.22	2	19.22	1	60.25	1
2	60.01	2	26.17	1	76.78	2
3	61.78	2	50.05	1	88.10	1
4	77.63	2	55.88	1	90.83	2
5	85.85	2	79.84	1	92.99	2
6	87.17	2	84.92	1	93.50	2
7	90.57	2	88.08	1	108.01	2
8	102.25	2	100.24	1	119.37	2
9	103.08	1	106.00	1	119.78	2
10	108.83	2	106.44	1	124.86	1
11	111.95	2	120.15	1	127.26	2
12	111.84	1	122.39	1	129.87	2
13	114.25	2	126.15	1	137.96	2
14	114.89	2	131.94	1	139.68	2
15	117.02	2	132.58	1	142.15	2
16	122.27	2	134.75	1	142.03	2
17	122.54	2	135.68	1	151.70	1
18	127.40	2	135.95	1	153.67	1
19	127.62	2	136.44	1	153.80	2
20	128.82	2	140.70	1	157.36	2
21	131.53	2	145.53	1	168.50	2
22	136.91	2	144.93	1	168.75	1
23	138.88	2	145.23	1	242.22	2
24	139.29	2	148.43	1	283.58	1
25	140.29	2	148.63	1		
26	142.00	2	148.63	1		
27	147.43	2	152.73	1		
28	148.27	1	153.97	1		
29	148.82	2	154.52	1		
30	149.16	2	156.49	1		
31	150.30	2	156.38	1		
32	150.64	2	156.50	1		
33	151.10	1	157.19	1		
34	153.90	2	160.69	1		
35	154.90	2	160.35	1		
36	156.09	2	161.23	1		
37	160.19	2	162.29	1		
38	162.62	2	168.10	1		
39	162.85	2	238.89	1		
40	163.02	2	262.85	1		
41	166.19	2	303.32	1		
42	258.33	2				
43	299.45	1				
44	414.00	1				