Supporting Information

Rational Design of Chiral Nanoscale Adamantanoids

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6 [2,2-Bis(4-(*trans*-Pt(PEt$_3$)$_2$(OTf))phenyl)propane] + 4 [2-(R)-phenyl[tris(4-pyridyl) methyl]butyrate] (6). An nmr tube containing 14.3 mg (0.0105 mmol) of **1** dissolved in 1 ml deuterated methylene chloride had added to it a solution of 2.7 mg (0.0066 mmol) of **2** in 0.5 ml deuterated methylene chloride. This reaction was done via titration of the solution of **1** with the solution of **2** under NMR monitoring. Yield: 100% (*via* nmr). MP: 220°C (dec.).

^{1}H NMR (CD_2Cl_2, 300 MHz) δ 8.68 (bs, 24H, $H_{\alpha pyr}$), 7.74 (bs, 24H, $H_{\beta pyr}$), 7.37 (bs, 20H, C(O)-CH-C_6H_5), 7.13 (bs, 24H, Pt-Ph-H_o), 6.86 (bs, 24H, Pt-Ph-H_m), 4.07 (m, 4H, C(O)-C*H*), 2.12 (m, 4H, C(O)-CH(Ph)- C*H*H), 1.87 (m, 4H, C(O)-CH(Ph)-CH*H*), 1.60 (s, 36H, Pt-Ph-C-CH_3), 1.26 (m, 144H, P-CH_2), 1.04 (m, 216H, P-CH_2-CH_3), 0.86 (m, 12H, C(O)-CH(Ph)-CH_2-CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz) δ 14.3 (s, ^{195}Pt satellites, J_{Pt-P} = 2670 Hz); ^{19}F NMR (CD_2Cl_2) δ -78.6; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 172.4(s, CO_{ester}), 153.1 (s, C_α), 147.4 (s, $C_{ipso\text{-}pyr}$), 138.1 ($C_{ipso\text{-}phenyl(ester)}$), 135.5 (s, Pt-$C_p$), 129.5, 128.9, 128.5 ($C_{phenyl(ester)}$), 127.4 (s, Pt-$C_o$), 126.8 (s, Pt-$C_{ipso}$), 123.7 (s, C_β), 119.5 (s, Pt-C_m), 113.0 (q, $J_{C\text{-}F}$ = 332 Hz, OTf), 88.1 (s, *C*(py)$_3$), 42.1 (s, Pt-Ph-*C*), 30.2 (s, Pt-Ph-C-*C*H_3), 25.7 (s, CH_2), 12.9 (bt, P-*C*H_2), 12.1 (s, CH_3), 8.0 (s, P-CH_2*C*H_3); Anal. Calcd for $C_{350}H_{536}F_{36}N_{12}O_{44}P_{24}Pt_{12}S_{12}$: C, 43.03; H, 5.53; N, 1.72; S, 3.94. Found: C, 41.92; H, 5.39; N, 1.82; S, 3.79.

6 [4,4'-Bis(*trans*-Pt(PEt_3)$_2$(OTf))benzophenone] + 4 [2-(R)-phenyl[tris(4-pyridyl)methyl] butyrate] (7). 5.3 mg (0.0040 mmol) of 4,4'-Bis(*trans*-Pt(PEt_3)$_2$(OTf))benzophenone were dissolved in 0.55 ml CD_2Cl_2. By titration with a solution of 1.1 mg (0.0027 mmol) of 2-(R)-phenyl[tris(4'–pyridyl)methyl]butyrate (**2**) in 0.45 ml CD_2Cl_2, adamantanoid **7** forms instantaneously in 100 % yield according to NMR-data. MP: 230°C (dec.).

^{1}H NMR (CD_2Cl_2, 300 MHz) δ 8.75 (bs, 24H, $H_{\alpha pyr}$), 7.82 (bs, 24H, $H_{\beta pyr}$), 7.51 (bs, 24H, Pt-Ph-H_o), 7.48 (bs, 24H, Pt-Ph-H_m), 7.39 (bs, 20H, C(O)-CH-C_6H_5), 4.08 (m, 4H, C(O)-C*H*), 2.16 (m, 4H, C(O)-CH(Ph)- CH*H*), 1.88 (m, 4H, C(O)-CH(Ph)- C*H*H), 1.34 (m, 144H, P-CH_2), 1.11 (m, 216H, P-CH_2-CH_3), 0.89 (m, 12H, C(O)-CH(Ph)-CH_2-CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz) δ 15.6 (s, ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2643 Hz); ^{19}F NMR (CD_2Cl_2) δ -78.6; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 197.3 (s, CO_{keton}), 173.1(s, CO_{ester}), 153.3 (s, C_α), 151.3 (s, $C_{ipso\text{-}pyr}$), 141.7 (s, Pt-C_m), 138.2 ($C_{ipso\text{-}phenyl(ester)}$), 136.6 (s, Pt-$C_o$), 134.0 (s, Pt-$C_p$), 130.0 (s, Pt-$C_{ipso}$), 129.6, 129.0, 128.6 ($C_{phenyl(ester)}$), 127.3 (s, C_β), 121.7 (q, $J_{C\text{-}F}$=322 Hz, OTf), 86.3 (s, *C*(py)$_3$), 25.9 (s, CH_2), 13.0 (bt, P-*C*H_2), 12.2 (s, CH_3), 8.0 (s, P-CH_2*C*H_3) Anal. Calcd for $C_{338}H_{500}F_{36}N_{12}O_{50}P_{24}Pt_{12}S_{12}$: C, 41.91; H, 5.21; N, 1.74; S, 3.96. Found: C, 41.11; H, 5.06; N, 1.84; S, 3.74.

Table 1: Electrospray Ionization Mass Spectrometric Data for Adamantanoids **6** and **7**.

adamantanoid 6	Fragment	m/z (Calculated)	m/z (Observed)	Charge
	2 **1** + 2 **2** + 3 OTf	3378	3380	+1
	4 **1** + 4 **2** + 6 OTf	3378	3380	+2
	4 **1** + 3 **2** + 6 OTf	3173	3176	+2
	(M - 3 OTf)	3105	3107	+3
	5 **1** + 4 **2** + 7 OTf	2654	2655	+3
	3 **1** + 2 **2** + 4 OTf	2292	2293	+2
	(M - 4 O Tf)	2292	2293	+4
	4 **1** + 3 **2** + 5 OTf	2066	2067	+3
	5 **1** + 4 **2** + 6 OTf	1953	1954	+4
	(M-5 O Tf)	1804	1805	+5
	n **1** + n **2** + n OTf	1615	1616	+n
	4 **1** + 4 **2** + 3 OTf	1262	1264	+5
	1 **1** + 0 **2** + 1 OTf	1205	1206	+1
	1 **1** + 2 **2** + 0 OTf	937	938	+2

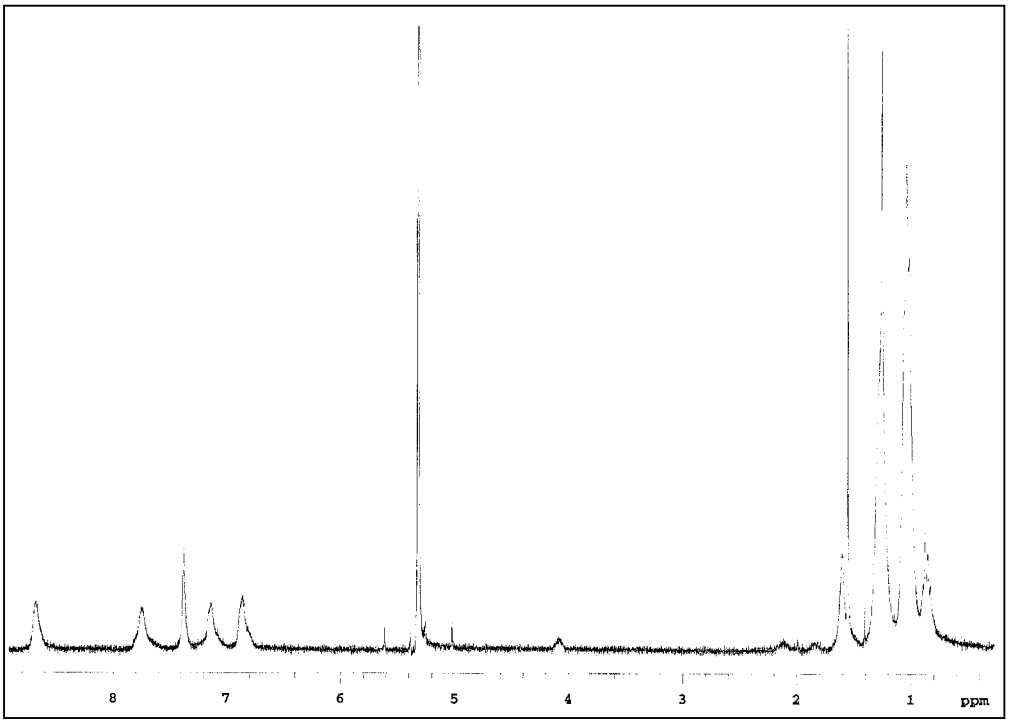
(M: intact cage **6**; ditopic linker **1**; tritopic linker **2**; OTf: triflate counterion)

adamantanoid 7	Fragment	m/z (Calculated)	m/z (Observed)	Charge
	4 **3** + 3 **2** + 6 OTf	3145	3147	+2
	$(M - 3\ OTf)^{3+}$	3077	3079	+3
	4 **3** + 2 **2** + 6 OTf	2943	2943	+2
	5 **3** + 4 **2** + 7 OTf	2632	2633	+3
	$(M - 4\ OTf)^{4+}$	2270	2272	+4
	3 **3** + 2 **2** + 4 OTf	2270	2272	+2
	4 **3** + 3 **2** + 5 OTf	2048	2049	+3
	5 **3** + 4 **2** + 6 OTf	1936	1937	+4
	$(M - 5\ OTf)^{5+}$	1787	1788	+5
	1 **3** + 1 **2** + 1 OTf	1602	1601	+1
	3 **3** + 4 **2** + 2 OTf	1265	1266	+4
	1 **3** + 1 OTf	1191	1192	+1
	2 **3** + 3 **2** + 1 OTf	1154	1155	+3
	1 **3** + 2 **2**	930	931	+2

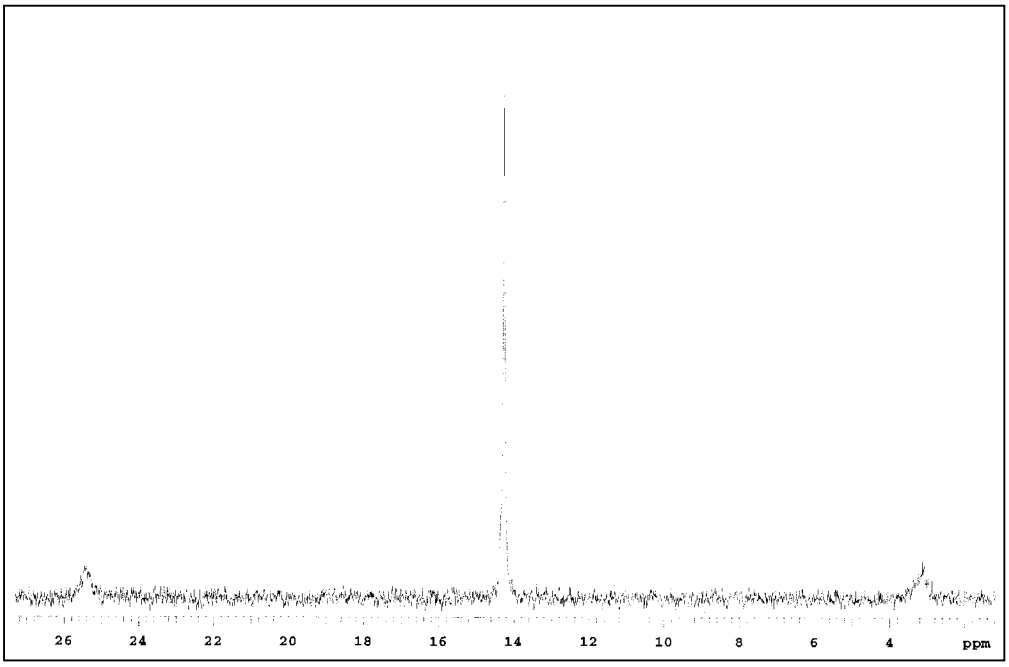
(M: intact cage **7**; ditopic linker **3**; tritopic linker **2**; OTf: triflate counterion)

Figure S1: ^{1}H NMR and ^{31}P NMR $\{^{1}H\}$ of adamantanoids **6** (A, B) and **7** (C, D).

300 MHz, CD_2Cl_2
A

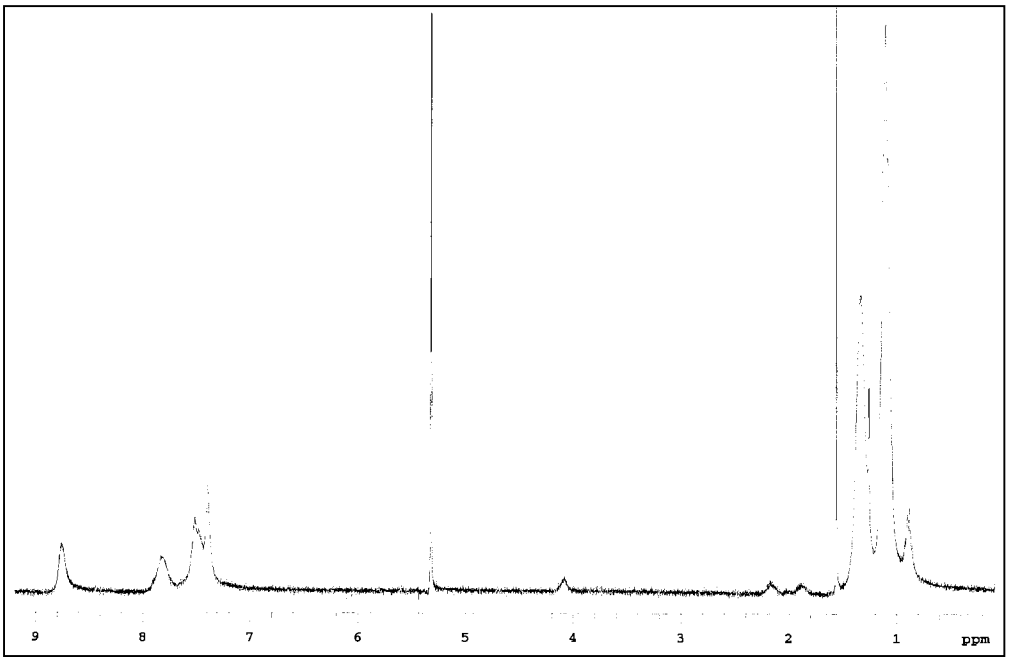


121 MHz, CD_2Cl_2
B



300 MHz, CD_2Cl_2

C



121 MHz, CD_2Cl_2

D