

Electronic Supplementary Information

Dioxygen insensitive C₇₀/AuNPs hybrid system for rapid and quantitative glucose biosensing

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61-Ethylloxycarbonyl-61-[8-(acetylthio)octyl-1-oxycarbonyl]-1,2-methano[60]fullerene (OT-C₇₀)

Yield: 17%, overall yield of the preformed addition reaction was significantly lowered by reaction of *S*-acetyl protecting group with DBU and formation of a corresponding thiol,¹ the mass spectrum (ESI-MS) showed a [M+Na]⁺ peak at 1179.5 (see Electronic Supplementary Information (ESI)), Fig. S1,); IR (KBr disk) $\nu_{\text{max}}(\text{cm}^{-1})$ 2922.6, 2848.8, 1743.2, 1686.5, 1427.3, 1225.7, 1134.3, 1092.2, 794.4, 670.1, 620.6, 576.8, 533.1, 457.4, see (see ESI, Fig. S2); $\delta^1\text{H}$ (500 MHz; CDCl₃; TMS) 4.49-4.54 (q, mH), 4.43-4.46 (m, 2H), 2.86 (t, 2H), 2.32 (s, 3H), 1.81 – 1.84 (m, 2H), 1.54-1.58 (m, 4H), 1.48 (t, 3H), 1.35-1.39 (m, 6H) ppm (see ESI, Fig. S3); $\delta^{13}\text{C}$ (125 MHz; CDCl₃) 196.02, 163.57, 163.48, 155.11, 155.08, 151.38, 151.36, 151.17, 150.73, 150.71, 150.58, 149.35, 149.26, 148.71, 148.70, 148.57, 148.51, 148.48, 147.65, 147.00, 146.45, 145.94, 145.91, 144.90, 144.83, 143.95, 143.94, 143.85, 143.84, 143.53, 143.00, 142.87, 142.83, 142.28, 142.17, 141.67, 141.65, 140.83, 140.72, 137.02, 136.91, 133.57, 132.83, 132.82, 130.93, 130.89, 130.81, 67.47, 63.52, 30.70, 29.52, 29.12, 29.10, 29.07, 28.76, 28.55, 25.95, 14.28 ppm (see ESI, Fig. S4).

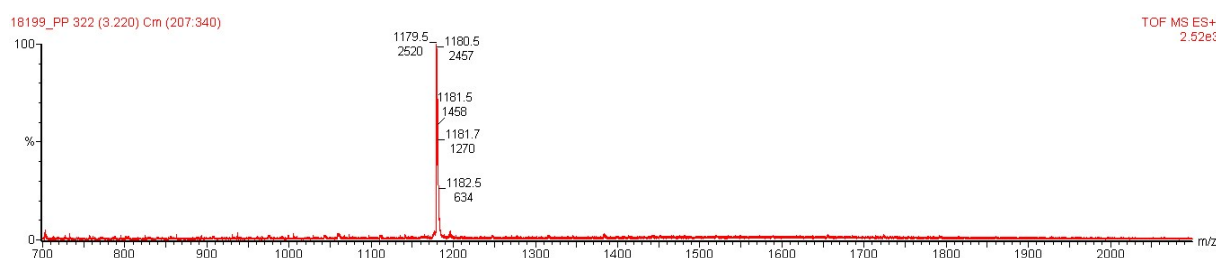


Fig. S1 ESI-MS spectrum of 61-Ethylloxycarbonyl-61-[8-(acetylthio)octyl-1-oxycarbonyl]-1,2-methano[70]fullerene (OT-C₇₀) as a [M + Na]⁺ cation.

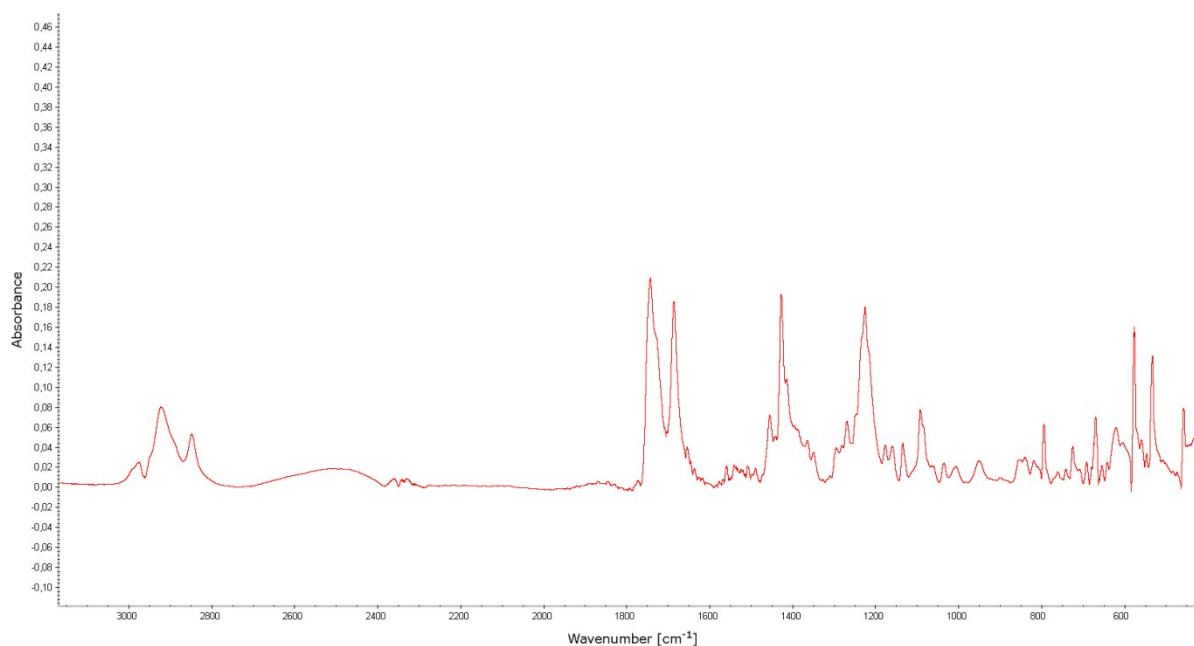


Fig. S2 IR spectrum of 61-Ethylloxycarbonyl-61-[8-(acetylthio)octyl-1-oxycarbonyl]-1,2-methano[70]fullerene (**OT-C₇₀**) in KBr disk.

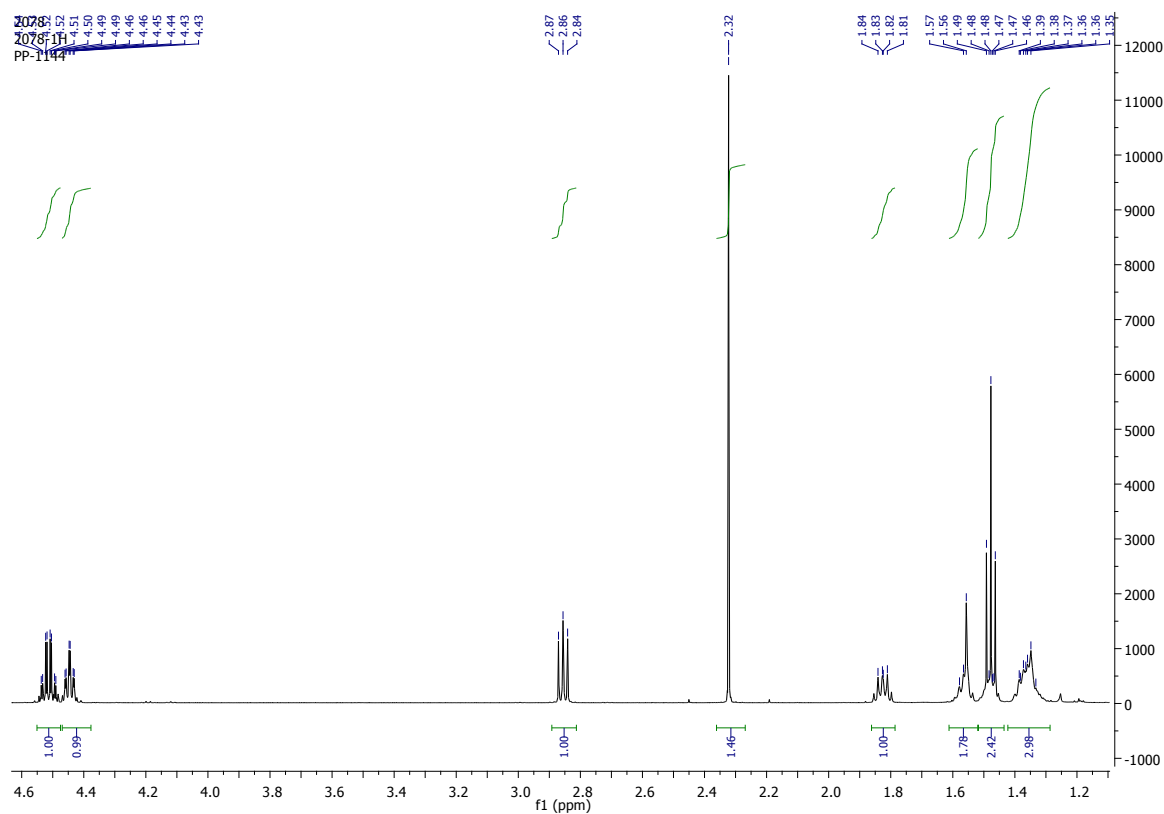


Fig. S3 ¹H NMR spectrum of 61-Ethylloxycarbonyl-61-[8-(acetylthio)octyl-1-oxycarbonyl]-1,2-methano[70]fullerene (**OT-C₇₀**) in CDCl₃.

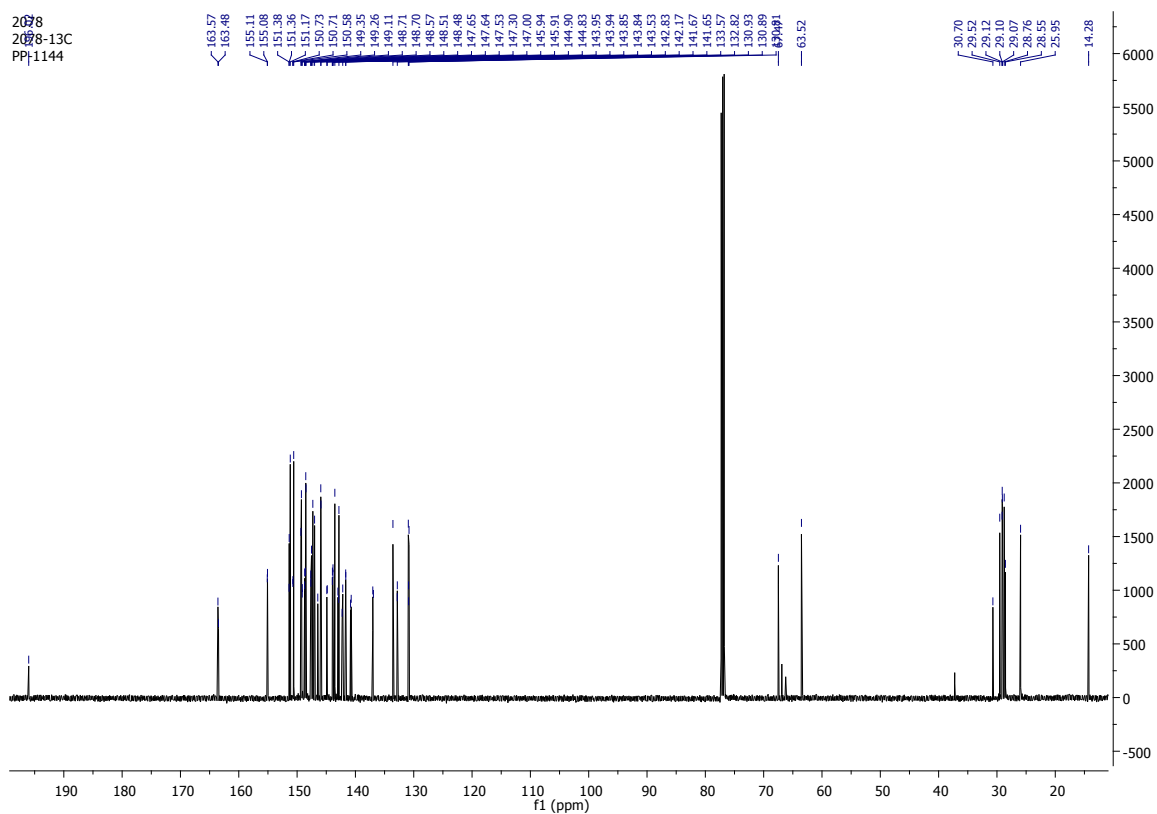


Fig. S4 ^{13}C NMR spectrum of 61-Ethylloxycarbonyl-61-[8-(acetylthio)octyl-1-oxycarbonyl]-1,2-methano[70]fullerene (**OT-C₇₀**) in CDCl_3 .

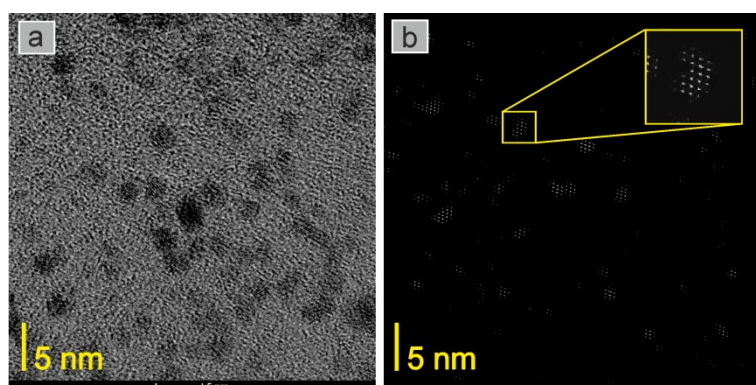


Fig. S5 High-resolution TEM image of **OT-C₇₀@AuNPs** (a) and its Fast Fourier Transform (FFT) image (b).

	Size (d.nm):	% Number:	St Dev (d.nm):
Peak 1:	17.47	100.0	3.587
Peak 2:	77.76	0.0	18.85
Peak 3:	0.000	0.0	0.000

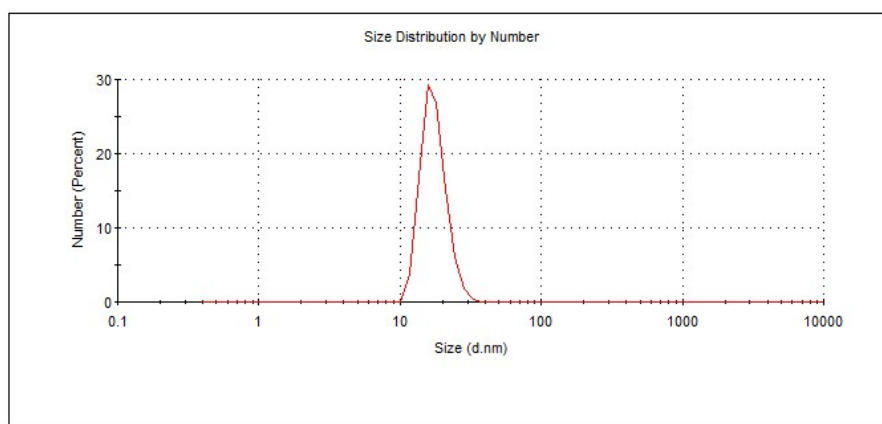


Fig. S6 Size distribution of synthesized bare **octanethiol-AuNPs** obtained from DLS measurements.

	Size (d.nm):	% Number:	St Dev (d.nm):
Peak 1:	21.39	100.0	5.765
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

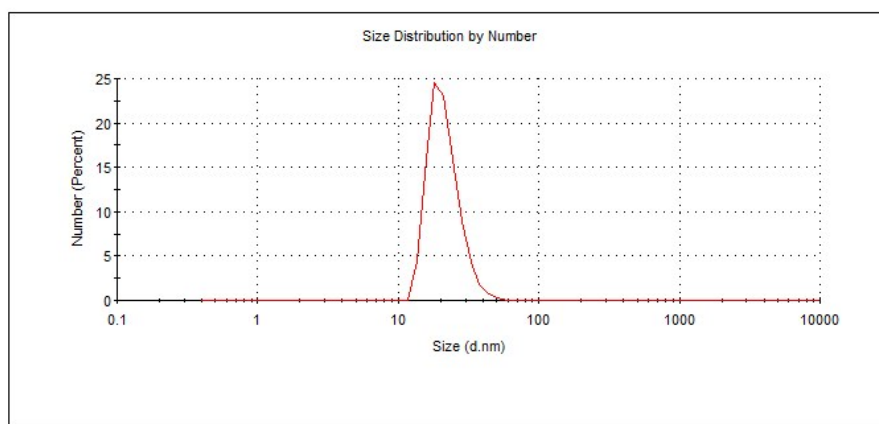


Fig. S7 Size distribution of AuNPs coated with the C_{70} fullerene derivative **OT- C_{70}** obtained from DLS measurements.

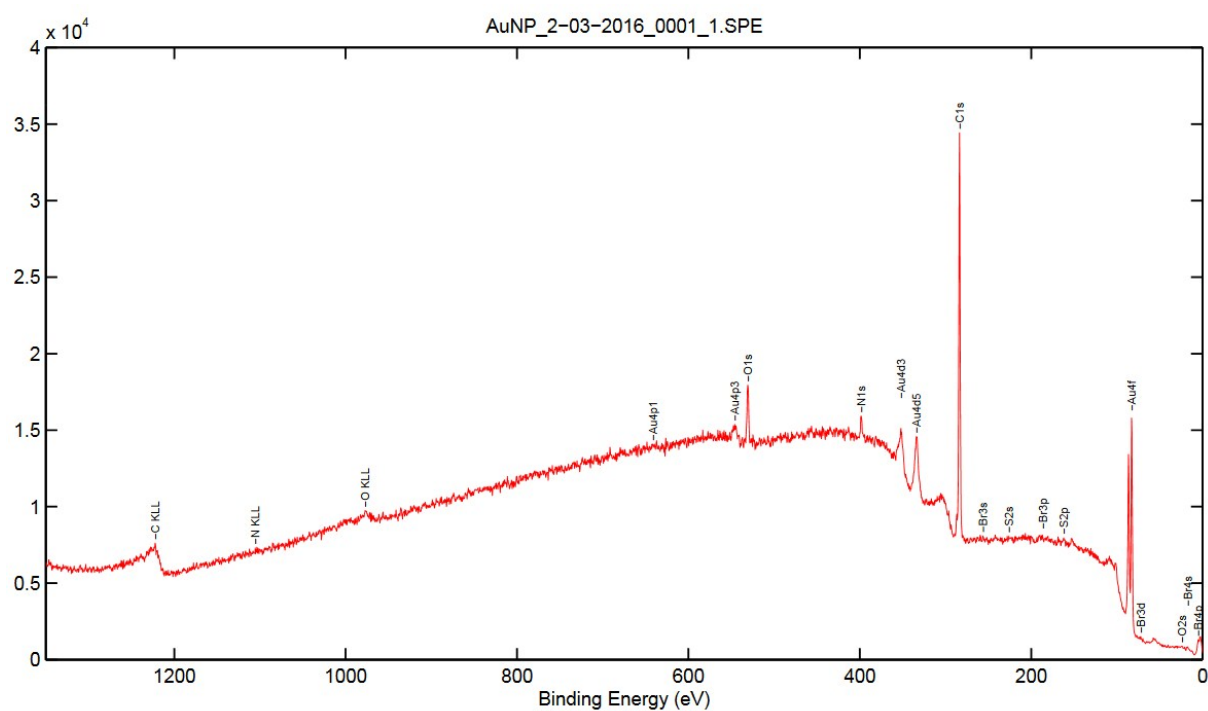


Fig. S8 XPS survey spectrum of gold nanoparticles functionalized with the C_{70} fullerene derivative **OT- C_{70}** .

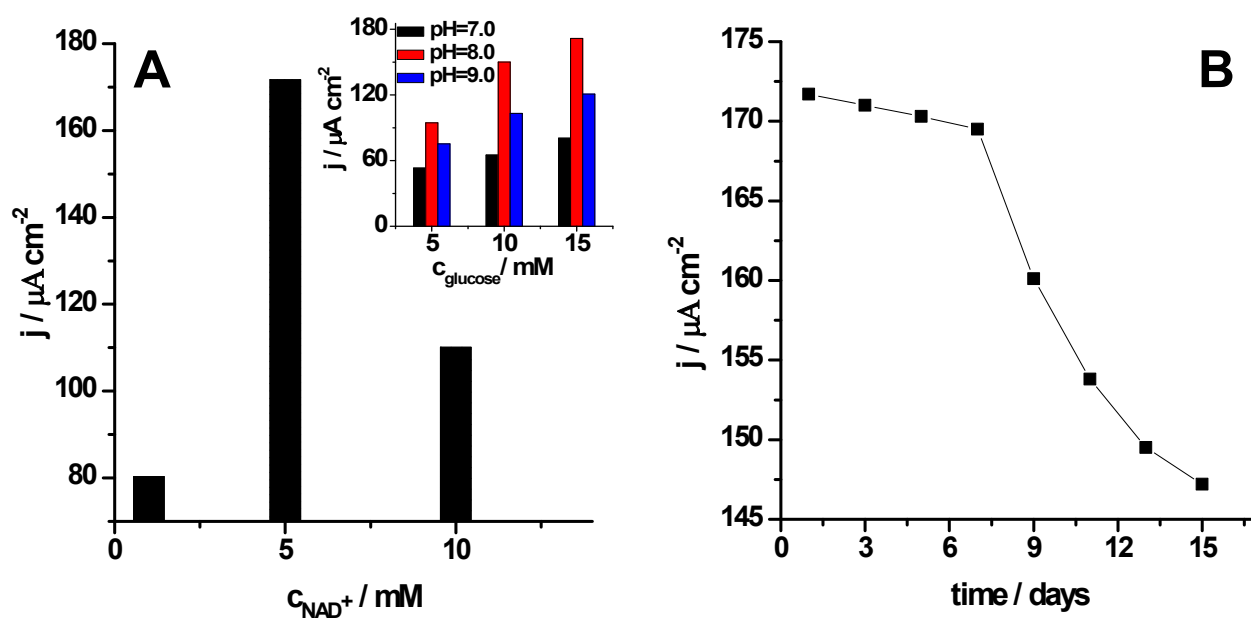


Fig. S9 (A) Effect of the different concentration of NAD^+ containing 15 mM glucose. Electrolyte: 0.1 M phosphate buffer solution at pH=8.0, scan rate: 5 mV s^{-1} . Inset: effect of

0.1 M phosphate buffer solution pH on the sensor response with different concentration of glucose (5, 10, 15mM) at scan rate 5 mV s⁻¹. (B) Stability measurements of **OT-C₇₀@AuNPs - GDH** film modified GCE in the presence of 15 mM glucose.

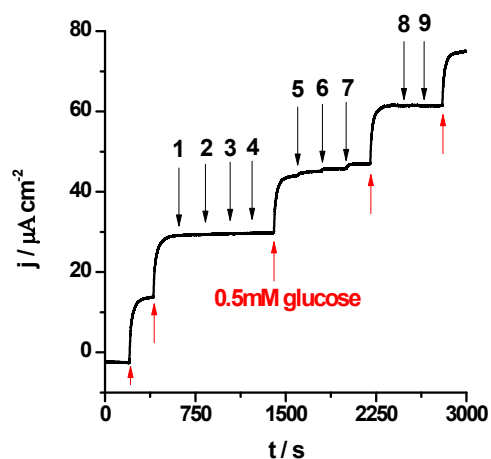


Fig. S10 Typical steady-state current response of **OT-C₇₀@AuNPs-GDH** modified GC electrode at E=0.7 V during addition of 0.5 mM glucose (red arrows) and interfering compounds such as: 1) 0.1 mM fructose, 2) 0.1 mM cellobiose, 3) 0.1 mM lactose, 4) 0.1 mM galactose, 5) 0.01 mM ascorbic acid, 6) 0.01 mM uric acid, 7) 0.01 mM dopamine, 8) Zn²⁺ ions, 9) Cu²⁺ ions. Electrolyte: deoxygenated 0.1 M PBS at pH=8.0 containing 5 mM NAD⁺.



Fig. S11 High-resolution TEM image of another batch of synthesized **OT-C₇₀@AuNPs** (a) and its FFT image (b).

Table S1 Comparison of the electrochemical properties of OT-C₇₀ and its assembly on the AuNPs surface.

	OT-C ₇₀ [V]	OT-C ₇₀ @AuNPs [V]
E _{pc1}	-0.626	-0.513
E _{pa1}	-0.462	-0.259
E ₁ ^{0'}	-0.544	-0.386
E _{pc2}	-1.064	-0.913
E _{pa2}	-0.795	-0.708
E ₂ ^{0'}	-0.930	-0.811
E _{pc3}	-1.593	-
E _{pa3}	-1.255	-
E ₃ ^{0'}	-1.424	-
E _{pc4}	-2.050	-
E _{pa4}	-1.691	-
E ₄ ^{0'}	-1.871	-

References

1. A. Singh, D.H. Dahanayaka, A. Biswas, L.A. Bumm and R.L. Halterman, *Langmuir*, 2010, **26**, 13221-13226.