Supplementary information

Design of Fulleropyrrolidine Derivatives as an Acceptor Molecule in the Thin Layer Organic Solar Cell

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Preparation of the solar cell:

Photovoltaic devices were prepared by spin-coating the fulleropyrrolidine-polymer blends from chlorobenzene on to an indium tin oxide (ITO) glass electrode as follows: To a P3HT (1.0 wt%) solution of chlorobenzene were added fulleropyrrolidine **1** (equal weight vs. P3HT) and silica gel (1.0 wt % vs. P3HT solution), then the mixture was stirred for 12 h at ambient temperature. It was then filtered through a Teflon (0.2 mm) filter. The resulting solution was applied to the surface of an ITO plate by the spin-coating method at a thickness of ca. 100 nm, and the surface was washed with acetone and irradiated under UV light and ozone gas for 20 min to decompose the impurities. After drying under vacuum for 20 min, the resulting plate was placed in a vacuum chamber and the surface was coated with the electrode layers of lithium fluoride (LiF) (4 nm) and aluminum (100 nm) by evaporation at 10^{-4} Pa at rt. We placed the glass plate on the resulting film and these plates were firmly fixed using a bonding agent under an argon atmosphere to produce the solar cell. The PCE values were obtained using the solar simulator OTENTO-SUN II (AM1.5G, 100 mW/cm^2).

Table S1. Characteristic Current-Voltage parameters of P3HT polymer blended with fullerene derivatives under standard AM 1.5G conditions

Fullerene	PCE (%)	J_{SC} (mA/cm^2)	V_{oc} (V)	FF	Lot # of P3HT (Aldrich)
PCBM	2.88	7.46	0.577	0.668	08510JJ
1p	3.32	7.61	0.66	0.66	08510JJ
PCBM	2.68	7.29	0.557	0.66	08510JJ
1p	3.38	7.82	0.641	0.674	08510JJ
PCBM	2.65	6.77	0.595	0.658	09007KH
1p	3.30	7.35	0.657	0.683	09007KH
PCBM	2.58	6.87	0.584	0.643	09007KH

Supplementary information

1p	3.44	7.84	0.661	0.663	09007KH
PCBM	2.53	6.85	0.583	0.633	08510JJ
1p	3.44	7.85	0.660	0.662	08510JJ

Average PCE for p3HT/[C60]-PCBM= 2.66±0.13 %; Average PCE for P3HT/**1p**=3.38±0.065%

Computational analysis:

DFT calculation of fulleropyrrolidine derivatives, **1a**, **1p**, **1q**, **1r**, **1x**, **1y**, and **2**, were performed at the B3LYP/6-31G* level of theory. All of the calculations were carried out with the Gaussian 03 suite of programs. Optimized coordinates of atoms, the energy for the molecular electronic state, and the eigenvalues of the HOMO's & the LUMO's in each of the molecules.

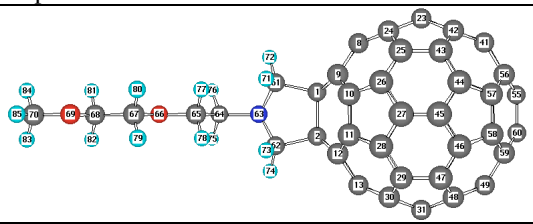
Table S2. Energy eigenvalues by DFT calculation (B3LYP/6-31G*) and V_{oc} 's for each of the fulleropyrrolidine derivatives

	Energy eigenvalue / Hartree		ΔE / eV vs. **2**		
Compound	HOMO	LUMO	HOMO	LUMO	V_{oc} / V
2	-0.20708	-0.11354	0.000	0.000	0.562
1a (C_6H_5)	-0.20606	-0.11264	0.028	0.024	0.599
1x (2-naphthyl)	-0.20588	-0.11250	0.033	0.028	0.659
1y (1-naphthyl)	-0.20505	-0.11251	0.055	0.028	0.637
1p (2-MeO)	-0.20366	-0.11050	0.093	0.083	0.660
1q (3-MeO)	-0.20465	-0.11141	0.066	0.058	0.635
1r (4-MeO)	-0.20513	-0.11181	0.053	0.047	0.639

Optimized coordinates of atoms, the energy for the molecular electronic state, and the eigenvalues of the HOMO's & the LUMO's in each of the molecules, by using B3LYP/6-31G* calculations.

Supplementary information

Compound **2**

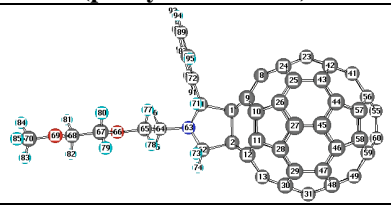


nuclear repulsion energy / Hartree: 10679.572354
E(RB+HF-LYP) / Hartree: -2767.110378
E(HOMO) / Hartree: -0.20708
E(LUMO) / Hartree: -0.11354

C1	-2.103013	0.771289	-0.256732	C44	2.931195	1.473666	3.006719
C2	-2.095818	-0.836622	-0.105341	C45	2.181567	0.335479	3.514676
C3	-1.271144	-1.564452	-1.174650	C46	2.942080	-0.870675	3.227642
C4	-0.778993	-0.971518	-2.315495	C47	2.278473	-2.046246	2.870496
C5	-0.785815	0.502316	-2.454213	C48	2.802000	-2.876191	1.797103
C6	-1.284870	1.293897	-1.444242	C49	3.966267	-2.497263	1.126019
C7	-0.567329	2.481431	-1.063378	C50	4.048604	-2.632893	-0.319703
C8	-0.649383	2.619897	0.379488	C51	4.789407	-1.495220	-0.835477
C9	-1.419286	1.519057	0.891795	C52	4.415368	-0.910197	-2.047275
C10	-1.045274	0.929593	2.080541	C53	4.408684	0.539342	-2.184032
C11	-1.038469	-0.545512	2.219529	C54	4.776519	1.344096	-1.103381
C12	-1.406818	-1.350357	1.162540	C55	5.159382	0.733492	0.158560
C13	-0.626412	-2.520660	0.864328	C56	4.642518	1.563594	1.233777
C14	-0.543885	-2.653402	-0.578916	C57	4.146087	0.970133	2.396333
C15	0.619353	-3.161107	-1.168239	C58	4.152732	-0.479257	2.532847
C16	1.124386	-2.548752	-2.372774	C59	4.655707	-1.275345	1.501540
C17	0.438384	-1.461549	-2.925546	C60	5.165348	-0.656066	0.289595
C18	1.182145	-0.324967	-3.438372	C61	-3.623948	1.099553	-0.386190
C19	0.427481	0.880534	-3.146188	C62	-3.613569	-1.197213	-0.172185
C20	1.103372	2.058132	-2.807685	N63	-4.187702	-0.113566	-0.947896
C21	0.592004	2.879846	-1.738128	C64	-5.619566	-0.144115	-1.209323
C22	1.720803	3.411829	-0.991052	C65	-6.550115	-0.026905	0.008307
C23	1.642206	3.543472	0.394629	O66	-7.875881	-0.063347	-0.483425
C24	0.430672	3.147841	1.095184	C67	-8.854995	0.039813	0.533621
C25	0.808732	2.543131	2.349078	C68	-10.222004	-0.018963	-0.132401
C26	0.086429	1.442169	2.823005	O69	-11.193703	0.122271	0.883031
C27	0.790202	0.319882	3.416951	C70	-12.514319	0.081480	0.386530
C28	0.096928	-0.900016	3.043941	H71	-4.020041	1.347472	0.616333
C29	0.829537	-2.063555	2.783587	H72	-3.805370	1.958095	-1.041108
C30	0.458166	-2.895360	1.665062	H73	-4.008976	-1.260056	0.858709
C31	1.673801	-3.403901	1.049964	H74	-3.786609	-2.163117	-0.658041
C32	1.752502	-3.533383	-0.335894	H75	-5.852574	-1.080595	-1.730069
C33	2.963852	-3.142239	-1.035941	H76	-5.858684	0.671490	-1.902194
C34	2.573625	-2.531776	-2.296842	H77	-6.369376	0.913573	0.555033
C35	3.286271	-1.436576	-2.789634	H78	-6.381263	-0.854816	0.716866
C36	2.576052	-0.313057	-3.379725	H79	-8.758743	-0.782624	1.260426
C37	3.275704	0.907385	-3.010819	H80	-8.753488	0.987074	1.087074
C38	2.552773	2.068926	-2.730979	H81	-10.304918	0.786972	-0.880228
C39	2.936177	2.907845	-1.606566	H82	-10.337341	-0.977830	-0.664190
C40	4.025080	2.551347	-0.808628	H83	-12.733449	-0.876763	-0.111572
C41	3.942711	2.687502	0.636887	H84	-12.705554	0.895498	-0.331203
C42	2.774675	3.175305	1.226219	H85	-13.184032	0.198125	1.242488
C43	2.257568	2.555546	2.436136				

Supplementary information

Compound **1a (phenyl substituent)**

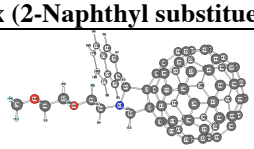


nuclear repulsion energy / Hartree: 12228.277519
E(RB+HF-LYP) / Hartree: -2998.161028
E(HOMO) / Hartree: -0.20606
E(LUMO) / Hartree: -0.11264

C1	-1.779872	0.380055	0.092564	C49	4.532096	-2.714256	-0.140805
C2	-1.652155	-1.103244	-0.523068	C50	4.590348	-2.155358	-1.481917
C3	-0.805552	-1.191145	-1.798793	C51	5.239571	-0.859039	-1.399610
C4	-0.383635	-0.103033	-2.527976	C52	4.798358	0.194657	-2.202924
C5	-0.493763	1.259563	-1.960847	C53	4.690018	1.536436	-1.648249
C6	-1.024889	1.451963	-0.704618	C54	5.027694	1.769255	-0.313266
C7	-0.378483	2.371912	0.193001	C55	5.480673	0.670329	0.522782
C8	-0.436968	1.818088	1.532360	C56	4.932971	0.864999	1.854929
C9	-1.117856	0.553748	1.463039	C57	4.506423	-0.235311	2.601802
C10	-0.676649	-0.492664	2.245424	C58	4.614446	-1.576982	2.047015
C11	-0.565545	-1.857786	1.681329	C59	5.145024	-1.762625	0.768715
C12	-0.901001	-2.099133	0.366637	C60	5.583785	-0.616111	-0.009010
C13	-0.051624	-2.938283	-0.434091	C61	-3.352507	0.601191	0.154022
C14	0.006317	-2.377888	-1.771741	C62	-3.135489	-1.511932	-0.769137
C15	1.186544	-2.469707	-2.518237	N63	-3.835663	-0.250540	-0.930322
C16	1.620423	-1.332747	-3.293064	C64	-5.277933	-0.344650	-1.148369
C17	0.849256	-0.164905	-3.282802	C65	-6.127680	-0.869131	0.018562
C18	1.501870	1.129003	-3.196875	O66	-7.459881	-0.938220	-0.453686
C19	0.674622	2.001575	-2.383378	C67	-8.379431	-1.396884	0.519302
C20	1.275990	2.930361	-1.527576	C68	-9.756909	-1.424870	-0.126769
C21	0.734734	3.119692	-0.204303	O69	-10.672365	-1.889506	0.843827
C22	1.841554	3.322819	0.716660	C70	-11.995058	-1.961641	0.356880
C23	1.786267	2.788756	2.003347	H71	-3.664018	0.211343	1.141675
C24	0.621158	2.027263	2.424204	C72	-3.810165	2.041713	0.063544
C25	1.068860	0.937033	3.255947	H73	-3.489349	-2.097343	0.098998
C26	0.434439	-0.306023	3.153682	H74	-3.247314	-2.136806	-1.661256
C27	1.227041	-1.522346	3.163688	H75	-5.440129	-1.001240	-2.011071
C28	0.610285	-2.474027	2.257844	H76	-5.655190	0.644275	-1.424816
C29	1.413513	-3.327512	1.493158	H77	-6.063162	-0.192071	0.886283
C30	1.073222	-3.566579	0.111614	H78	-5.788677	-1.864572	0.350631
C31	2.305788	-3.642142	-0.656487	H79	-8.113803	-2.406854	0.870842
C32	2.361116	-3.105263	-1.942252	H80	-8.393174	-0.731243	1.397097
C33	3.526415	-2.348247	-2.365393	H81	-10.024398	-0.414114	-0.476360
C34	3.066676	-1.250373	-3.201133	H82	-9.740042	-2.086850	-1.008351
C35	3.691216	-0.004079	-3.117855	H83	-12.078222	-2.654200	-0.496350
C36	2.892718	1.211261	-3.123795	H84	-12.366553	-0.974449	0.037737
C37	3.515508	2.165362	-2.220680	H85	-12.620422	-2.329098	1.174735
C38	2.722236	3.008371	-1.439397	C86	-3.886703	2.708085	-1.168259
C39	3.073927	3.252220	-0.049286	C87	-4.291517	4.040916	-1.227580
C40	4.202954	2.643543	0.502295	C88	-4.618003	4.730308	-0.057057
C41	4.144692	2.084388	1.843509	C89	-4.544038	4.076200	1.172775
C42	2.960419	2.157406	2.580022	C90	-4.147731	2.738534	1.229468
C43	2.515366	1.010238	3.355559	H91	-3.630850	2.170991	-2.076214
C44	3.274710	-0.161860	3.362743	H92	-4.350830	4.542919	-2.189610
C45	2.616057	-1.455521	3.273351	H93	-4.931758	5.769573	-0.104864
C46	3.449456	-2.331955	2.465526	H94	-4.800537	4.602362	2.088300
C47	2.859306	-3.249267	1.593641	H95	-4.097895	2.230443	2.190061
C48	3.412417	-3.443978	0.262938				

Supplementary information

Compound **1x (2-Naphthyl substituent)**

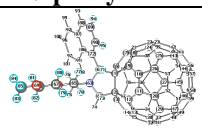


nuclear repulsion energy / Hartree: 13137.517305
E(RB+HF-LYP) / Hartree: -3151.804751
E(HOMO) / Hartree: -0.20588
E(LUMO) / Hartree: -0.11250

C1	-1.520203	-0.139059	0.186607	C52	4.974750	0.802560	-2.161518
C2	-1.232680	-1.493101	-0.638109	C53	4.721304	2.028956	-1.418959
C3	-0.413570	-1.295941	-1.919648	C54	5.061438	2.108897	-0.066653
C4	-0.142418	-0.072298	-2.487715	C55	5.662586	0.965838	0.599248
C5	-0.399964	1.172423	-1.729327	C56	5.128838	0.901771	1.949492
C6	-0.920649	1.119633	-0.454921	C57	4.854869	-0.336797	2.533632
C7	-0.364798	1.974567	0.560743	C58	5.107891	-1.562966	1.790650
C8	-0.322824	1.233108	1.806912	C59	5.625868	-1.500162	0.495297
C9	-0.849097	-0.082062	1.561895	C60	5.905761	-0.210002	-0.112789
C10	-0.268075	-1.167632	2.182640	C61	-3.105408	-0.125919	0.295026
C11	-0.009603	-2.414957	1.426965	C62	-2.662910	-2.037404	-0.931476
C12	-0.346658	-2.506544	0.093557	N63	-3.511726	-0.859351	-0.901425
C13	0.577405	-3.113343	-0.825265	C64	-4.937911	-1.099852	-1.116399
C14	0.534228	-2.367181	-2.069467	C65	-5.684494	-1.884742	-0.027364
C15	1.698843	-2.207932	-2.829125	O66	-7.007800	-2.064341	-0.495187
C16	1.974996	-0.928900	-3.436019	C67	-7.837317	-2.758594	0.417309
C17	1.070816	0.123383	-3.252144	C68	-9.216853	-2.878977	-0.213600
C18	1.566738	1.461335	-2.985611	O69	-10.040533	-3.578092	0.696829
C19	0.661228	2.102861	-2.049659	C70	-11.356904	-3.753520	0.219101
C20	1.169190	2.966958	-1.074032	C71	-3.945043	2.065184	-0.654705
C21	0.641962	2.900105	0.266698	C72	-4.522212	3.353561	-0.511042
C22	1.739495	3.102275	1.198737	C73	-4.889179	3.811409	0.796699
C23	1.780113	2.388780	2.395633	C74	-4.663155	2.951696	1.903332
C24	0.724496	1.440255	2.711853	C75	-4.107851	1.704876	1.727569
C25	1.319331	0.305436	3.374684	C76	-3.736575	1.243075	0.436427
C26	0.834949	-0.978321	3.100192	C77	-4.747797	4.207914	-1.624828
C27	1.766476	-2.078553	2.928877	C78	-5.467128	5.101876	0.937299
C28	1.244779	-2.959918	1.900152	C79	-5.672095	5.904657	-0.161729
C29	2.125257	-3.592055	1.014988	C80	-5.308305	5.453320	-1.455233
C30	1.781884	-3.671657	-0.383980	H81	-3.338406	-0.697727	1.213550
C31	2.995276	-3.487783	-1.163819	H82	-2.924912	-2.779684	-0.155743
C32	2.954541	-2.771389	-2.359215	H83	-2.721706	-2.535476	-1.904676
C33	4.011035	-1.826921	-2.678366	H84	-5.042357	-1.644518	-2.061928
C34	3.402977	-0.685588	-3.343711	H85	-5.439684	-0.136629	-1.245263
C35	3.876716	0.602745	-3.087327	H86	-5.687447	-1.329172	0.924971
C36	2.939369	1.700707	-2.912378	H87	-5.211069	-2.862424	0.162762
C37	3.466725	2.585813	-1.886346	H88	-7.437884	-3.763109	0.630856
C38	2.597717	3.206506	-0.986402	H89	-7.911795	-2.218853	1.374838
C39	2.952077	3.290829	0.421719	H90	-9.618327	-1.874184	-0.424663
C40	4.158416	2.751483	0.871718	H91	-9.140630	-3.414269	-1.174478
C41	4.201229	2.005852	2.119510	H92	-11.376896	-4.334677	-0.717068
C42	3.034790	1.829062	2.866716	H93	-11.856636	-2.788376	0.036928
C43	2.748740	0.538618	3.472994	H94	-11.909149	-4.299967	0.988137
C44	3.641875	-0.521902	3.306117	H95	-3.665400	1.719773	-1.646112
C45	3.139921	-1.859961	3.036320	H96	-4.942598	3.290823	2.898023
C46	4.051991	-2.505259	2.105165	H97	-3.947171	1.057676	2.586684
C47	3.553667	-3.354409	1.114967	H98	-4.467158	3.859298	-2.615856
C48	4.093223	-3.290294	-0.233997	H99	-5.744763	5.445558	1.931065
C49	5.108353	-2.380677	-0.537225	H100	-6.113969	6.890115	-0.041777
C50	5.066269	-1.633894	-1.784338	H101	-5.474383	6.097410	-2.314449
C51	5.558126	-0.292969	-1.521157				

Supplementary information

Compound **1y (1-Naphthyl substituent)**

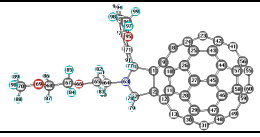


nuclear repulsion energy / Hartree: 13265.991882
E(RB+HF-LYP) / Hartree: -3151.798812
E(HOMO) / Hartree: -0.20505
E(LUMO) / Hartree: -0.11251

C1	-1.569598	0.026728	0.207675	C52	4.977674	0.905841	-2.017308
C2	-1.354684	-1.225264	-0.786253	C53	4.789492	2.036967	-1.120085
C3	-0.522424	-0.907603	-2.035490	C54	5.128586	1.920791	0.229816
C4	-0.176630	0.363333	-2.435326	C55	5.663055	0.668736	0.738331
C5	-0.366043	1.510375	-1.520224	C56	5.121824	0.458378	2.070728
C6	-0.898340	1.323266	-0.263490	C57	4.776616	-0.828926	2.487709
C7	-0.300594	2.005931	0.852930	C58	4.965296	-1.959870	1.590682
C8	-0.302095	1.105408	1.990174	C59	5.491001	-1.756733	0.312922
C9	-0.897853	-0.134872	1.575297	C60	5.843594	-0.415647	-0.121816
C10	-0.380765	-1.322623	2.047328	C61	-3.152488	0.091451	0.340039
C11	-0.188971	-2.473731	1.135626	C62	-2.812211	-1.664055	-1.125804
C12	-0.524617	-2.370806	-0.196848	N63	-3.613267	-0.468378	-0.930341
C13	0.365807	-2.903841	-1.191035	C64	-5.054833	-0.627058	-1.120256
C14	0.368017	-2.000140	-2.326573	C65	-5.802761	-1.489705	-0.092668
C15	1.543168	-1.806872	-3.061622	O66	-7.144787	-1.570043	-0.534534
C16	1.892564	-0.476440	-3.496420	C67	-7.983553	-2.290383	0.348931
C17	1.047388	0.590608	-3.173281	C68	-9.384031	-2.296603	-0.246167
C18	1.615242	1.852967	-2.736324	O69	-10.218564	-3.012043	0.641526
C19	0.743382	2.415407	-1.721155	C70	-11.556191	-3.082833	0.197087
C20	1.293252	3.117164	-0.643101	H71	-3.380149	-0.610799	1.163382
C21	0.757202	2.905229	0.678539	C72	-3.742054	1.429610	0.763985
C22	1.861148	2.922444	1.625481	H73	-3.097173	-2.488533	-0.447214
C23	1.858220	2.057472	2.718744	H74	-2.902536	-2.030622	-2.153377
C24	0.750903	1.134689	2.911112	H75	-5.213017	-1.063799	-2.113192
C25	1.279375	-0.108174	3.417751	H76	-5.514884	0.365473	-1.132928
C26	0.726361	-1.316397	2.978832	H77	-5.757282	-1.032148	0.908816
C27	1.596294	-2.435143	2.663360	H78	-5.365686	-2.499382	-0.015786
C28	1.031113	-3.144621	1.529751	H79	-7.629274	-3.325980	0.476540
C29	1.878389	-3.703220	0.566213	H80	-8.005622	-1.820419	1.345095
C30	1.536823	-3.579720	-0.829781	H81	-9.736382	-1.260300	-0.377541
C31	2.761558	-3.363143	-1.582873	H82	-9.363393	-2.768834	-1.242237
C32	2.764321	-2.495548	-2.674338	H83	-11.636542	-3.596780	-0.774463
C33	3.872348	-1.576685	-2.870694	H84	-12.005860	-2.081793	0.096434
C34	3.331404	-0.326337	-3.379411	H85	-12.115415	-3.649775	0.945999
C35	3.874283	0.889456	-2.957632	C86	-3.974380	2.549640	-0.110512
C36	2.998454	2.005629	-2.638267	C87	-4.490590	3.767182	0.456332
C37	3.569511	2.718619	-1.506424	C88	-4.758022	3.844720	1.848370
C38	2.732917	3.263314	-0.529708	C89	-4.537152	2.761644	2.662398
C39	3.085560	3.143199	0.875781	C90	-4.036833	1.561718	2.110785
C40	4.259283	2.484341	1.247522	C91	-3.735245	2.524956	-1.515160
C41	4.255605	1.580345	2.386421	C92	-4.730432	4.885659	-0.387020
C42	3.078312	1.372088	3.107900	H93	-5.145040	4.775977	2.255021
C43	2.718918	0.030912	3.540570	H94	-4.746897	2.816102	3.726862
C44	3.552980	-1.046317	3.233696	H95	-3.870331	0.714597	2.771983
C45	2.979282	-2.308141	2.793467	C96	-4.481992	4.823932	-1.737828
C46	3.857896	-2.875857	1.783015	C97	-3.982422	3.628105	-2.302535
C47	3.317606	-3.559861	0.691958	H98	-3.364741	1.611530	-1.962187
C48	3.865230	-3.349426	-0.638679	H99	-5.118674	5.796917	0.061938
C49	4.929087	-2.464411	-0.823859	H100	-4.670654	5.686695	-2.370913
C50	4.932889	-1.560091	-1.962596	H101	-3.790967	3.577249	-3.371129
C51	5.496943	-0.294495	-1.527802				

Supplementary information

Compound **1p (2-methoxyphenyl)**

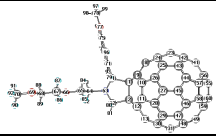


nuclear repulsion energy / Hartree: 12897.976301
E(RB+HF-LYP) / Hartree: -3112.683438
E(HOMO) / Hartree: -0.20366
E(LUMO) / Hartree: -0.11050

C1	-1.657008	0.224721	-0.124250	C51	5.452902	-0.980016	-1.153805
C2	-1.459546	-1.332451	-0.488719	C52	5.011677	-0.083356	-2.129674
C3	-0.562507	-1.591823	-1.706327	C53	4.840329	1.324251	-1.800043
C4	-0.141793	-0.617352	-2.582485	C54	5.116580	1.777404	-0.508278
C5	-0.315937	0.813026	-2.245021	C55	5.568574	0.841980	0.507514
C6	-0.901456	1.181894	-1.054608	C56	4.963733	1.225815	1.772141
C7	-0.320640	2.255969	-0.293813	C57	4.539709	0.242500	2.668775
C8	-0.416954	1.919525	1.113976	C58	4.711667	-1.165259	2.339732
C9	-1.057191	0.636649	1.223912	C59	5.299028	-1.531871	1.126692
C10	-0.614902	-0.255689	2.177614	C60	5.733230	-0.507660	0.191632
C11	-0.438582	-1.687259	1.842776	C61	-3.237020	0.399184	-0.164042
C12	-0.712434	-2.145419	0.572511	C62	-2.918683	-1.830687	-0.706653
C13	0.192101	-3.070335	-0.053452	N63	-3.652956	-0.643528	-1.106646
C14	0.284802	-2.728407	-1.461156	C64	-5.088484	-0.834472	-1.313556
C15	1.497378	-2.893249	-2.140578	C65	-5.936330	-1.135118	-0.068228
C16	1.927869	-1.878640	-3.071032	O66	-7.257572	-1.363628	-0.523325
C17	1.122051	-0.752888	-3.274125	C67	-8.177753	-1.600382	0.524888
C18	1.731172	0.561241	-3.373512	C68	-9.545440	-1.825140	-0.103240
C19	0.845403	1.520924	-2.739773	O69	-10.463726	-2.049039	0.947229
C20	1.383669	2.595216	-2.023375	C70	-11.777903	-2.274670	0.485244
C21	0.783881	2.972241	-0.766866	C71	-3.724256	1.782309	-0.542567
C22	1.846165	3.357971	0.147822	C72	-3.814743	2.177070	-1.880308
C23	1.755741	3.032234	1.500358	C73	-4.258392	3.451002	-2.237736
C24	0.598117	2.305605	1.996670	C74	-4.615247	4.353923	-1.239191
C25	1.045012	1.378266	3.007462	C75	-4.532562	3.990260	0.106305
C26	0.453219	0.112605	3.082097	C76	-4.088997	2.709636	0.456688
C27	1.281109	-1.057374	3.314650	H77	-3.584607	0.178669	0.856750
C28	0.730153	-2.162299	2.551189	H78	-3.285496	-2.269541	0.238929
C29	1.589528	-3.096006	1.960844	H79	-2.977437	-2.604187	-1.479416
C30	1.312747	-3.562919	0.624385	H80	-5.214402	-1.661119	-2.022367
C31	2.576883	-3.714768	-0.078077	H81	-5.496522	0.060748	-1.791819
C32	2.666801	-3.386476	-1.430069	H82	-5.916136	-0.286239	0.634471
C33	3.824777	-2.664246	-1.927682	H83	-5.561330	-2.019826	0.472792
C34	3.365892	-1.730082	-2.943260	H84	-7.889322	-2.485596	1.114427
C35	3.948766	-0.464733	-3.039112	H85	-8.222510	-0.741878	1.214035
C36	3.114965	0.704834	-3.267283	H86	-9.829439	-0.942731	-0.700048
C37	3.672239	1.812053	-2.506789	H87	-9.504063	-2.688731	-0.787325
C38	2.822263	2.738159	-1.898015	H88	-11.835468	-3.164257	-0.162682
C39	3.110004	3.211265	-0.553211	H89	-12.165874	-1.411085	-0.078911
C40	4.234044	2.739672	0.127529	H90	-12.406330	-2.435213	1.365247
C41	4.139706	2.398467	1.538154	H91	-3.532315	1.460034	-2.644724
C42	2.924425	2.543086	2.210874	H92	-4.321768	3.732136	-3.284720
C43	2.483166	1.518268	3.143582	H93	-4.961313	5.350895	-1.498561
C44	3.276826	0.390732	3.365192	H94	-4.813382	4.704970	0.871047
C45	2.662066	-0.923825	3.460198	O95	-3.978300	2.273675	1.749677
C46	3.554056	-1.886151	2.832508	C96	-4.305088	3.169132	2.801499
C47	3.027203	-2.950819	2.098280	H97	-4.133459	2.616312	3.726691
C48	3.639446	-3.333861	0.835897	H98	-5.356552	3.480880	2.753831
C49	4.751660	-2.636946	0.359934	H99	-3.662097	4.058342	2.785091
C50	4.846663	-2.295769	-1.050420				

Supplementary information

Compound **1q (3-methoxyphenyl)**

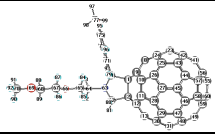


nuclear repulsion energy / Hartree: 12783.400031
E(RB+HF-LYP) / Hartree: -3112.684142
E(HOMO) / Hartree: -0.20465
E(LUMO) / Hartree: -0.11141

C1	-1.626346	0.074121	-0.062354	C51	5.511067	-0.859819	-1.169051
C2	-1.372408	-1.478861	-0.409690	C52	5.022958	0.005474	-2.150701
C3	-0.480483	-1.718227	-1.634878	C53	4.799655	1.409482	-1.837024
C4	-0.110414	-0.739327	-2.528814	C54	5.073712	1.890475	-0.554896
C5	-0.337365	0.687422	-2.208063	C55	5.575373	0.987474	0.466897
C6	-0.923497	1.049516	-1.015503	C56	4.971616	1.363961	1.734220
C7	-0.375441	2.155025	-0.275917	C57	4.598557	0.376500	2.648795
C8	-0.439694	1.834063	1.137129	C58	4.822191	-1.027626	2.335737
C9	-1.026101	0.528206	1.272024	C59	5.408429	-1.386742	1.120048
C10	-0.537209	-0.333419	2.231567	C60	5.789419	-0.358729	0.166207
C11	-0.308866	-1.761642	1.913189	C61	-3.211511	0.183609	-0.074842
C12	-0.580319	-2.247125	0.652530	C62	-2.813794	-2.037132	-0.604497
C13	0.352883	-3.143440	0.026637	N63	-3.599598	-0.881210	-0.996874
C14	0.414608	-2.816916	-1.386319	C64	-5.026472	-1.122024	-1.206997
C15	1.624011	-2.942392	-2.079410	C65	-5.861886	-1.472311	0.033474
C16	2.001701	-1.923774	-3.028423	O66	-7.170961	-1.752379	-0.426216
C17	1.149127	-0.833840	-3.234979	C67	-8.081652	-2.043698	0.617051
C18	1.703797	0.501850	-3.359675	C68	-9.436826	-2.319461	-0.017841
C19	0.788346	1.434004	-2.726773	O69	-10.345548	-2.603309	1.026186
C20	1.292177	2.538360	-2.031336	C70	-11.647024	-2.881486	0.556863
C21	0.693530	2.908151	-0.772317	C71	-3.765953	1.545452	-0.440329
C22	1.751249	3.348352	0.123422	C72	-3.844263	1.966636	-1.778734
C23	1.690850	3.037550	1.481136	C73	-4.341788	3.230962	-2.074762
C24	0.569796	2.271854	2.001767	C74	-4.761340	4.101098	-1.062854
C25	1.065788	1.376183	3.017831	C75	-4.682262	3.683604	0.269531
C26	0.525888	0.089271	3.117936	C76	-4.189506	2.404595	0.571211
C27	1.402717	-1.043633	3.354513	O77	-5.062967	4.433191	1.344500
C28	0.886935	-2.179841	2.612573	C78	-5.566724	5.738339	1.107632
C29	1.775499	-3.086272	2.022991	H79	-3.529185	-0.042231	0.960369
C30	1.500851	-3.581368	0.696186	H80	-3.150198	-2.487751	0.346932
C31	2.761113	-3.692568	-0.020625	H81	-2.852638	-2.814462	-1.374610
C32	2.820936	-3.379058	-1.377924	H82	-5.121709	-1.942965	-1.927150
C33	3.942588	-2.617943	-1.900033	H83	-5.464673	-0.234848	-1.673484
C34	3.434191	-1.716271	-2.921483	H84	-5.878925	-0.630270	0.744511
C35	3.964764	-0.430097	-3.041287	H85	-5.449034	-2.345730	0.565307
C36	3.081983	0.702059	-3.273561	H86	-7.755645	-2.923981	1.194200
C37	3.604001	1.840701	-2.534681	H87	-8.164681	-1.197768	1.317884
C38	2.725442	2.740415	-1.926830	H88	-9.759816	-1.440729	-0.600086
C39	3.010968	3.242645	-0.592117	H89	-9.354819	-3.168310	-0.716625
C40	4.161455	2.825223	0.080017	H90	-11.661952	-3.761644	-0.106214
C41	4.098351	2.499798	1.495989	H91	-12.073282	-2.027300	0.006185
C42	2.886902	2.604907	2.182614	H92	-12.269055	-3.085727	1.432306
C43	2.498882	1.575696	3.134018	H93	-3.521549	1.297873	-2.569127
C44	3.339334	0.483627	3.359109	H94	-4.407719	3.555035	-3.110076
C45	2.778918	-0.852964	3.479712	H95	-5.144775	5.081368	-1.321699
C46	3.700684	-1.787361	2.852868	H96	-4.146693	2.105595	1.614888
C47	3.207863	-2.882019	2.139574	H97	-5.797304	6.152859	2.090611
C48	3.819078	-3.257429	0.874401	H98	-6.481575	5.713913	0.500747
C49	4.896189	-2.522908	0.374945	H99	-4.822051	6.374566	0.611364
C50	4.959480	-2.197110	-1.040800				

Supplementary information

Compound **1r** (4-methoxyphenyl)



nuclear repulsion energy / Hartree: 12762.137163
E(RB+HF-LYP) / Hartree: -3112.684280
E(HOMO) / Hartree: -0.20513
E(LUMO) / Hartree: -0.11181

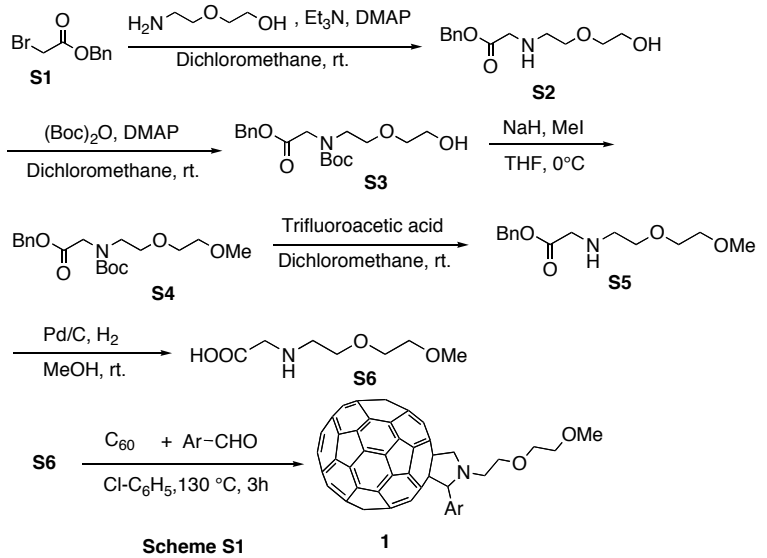
C1	-1.619386	-0.004940	0.111576	C51	5.481231	-0.469771	-1.436977
C2	-1.356035	-1.422712	-0.606237	C52	4.939574	0.591737	-2.165306
C3	-0.509925	-1.341278	-1.883770	C53	4.706719	1.874565	-1.517493
C4	-0.192966	-0.169111	-2.532016	C54	5.023994	2.042688	-0.167947
C5	-0.428235	1.133543	-1.869689	C55	5.580912	0.935195	0.590207
C6	-0.971227	1.185699	-0.604989	C56	5.021637	0.983024	1.930580
C7	-0.412589	2.097362	0.357659	C57	4.702632	-0.202641	2.596185
C8	-0.414964	1.447162	1.654454	C58	4.934780	-1.485224	1.947533
C9	-0.973314	0.132281	1.493036	C59	5.478064	-1.529559	0.661624
C10	-0.433630	-0.920713	2.201424	C60	5.804711	-0.294600	-0.031135
C11	-0.196323	-2.225929	1.542679	C61	-3.205333	0.067709	0.184082
C12	-0.510918	-2.403515	0.212769	C62	-2.797063	-1.949812	-0.880545
C13	0.411229	-3.100365	-0.641681	N63	-3.611642	-0.750860	-0.957198
C14	0.411161	-2.444759	-1.936670	C64	-5.040972	-0.961850	-1.179112
C15	1.593830	-2.371025	-2.681690	C65	-5.831239	-1.626187	-0.042132
C16	1.916807	-1.147045	-3.373128	O66	-7.164188	-1.757740	-0.499413
C17	1.039002	-0.060812	-3.284254	C67	-8.035096	-2.321536	0.462956
C18	1.567265	1.279636	-3.104651	C68	-9.426101	-2.378647	-0.151444
C19	0.663784	2.010097	-2.234249	O69	-10.292624	-2.943600	0.810934
C20	1.177235	2.928980	-1.312881	C70	-11.625226	-3.040364	0.356686
C21	0.623835	2.973208	0.018397	C71	-3.798962	1.458921	0.193135
C22	1.709121	3.212964	0.955818	C72	-3.944060	2.206994	-0.980142
C23	1.708310	2.586083	2.201006	C73	-4.477880	3.496553	-0.959995
C24	0.620947	1.691288	2.563169	C74	-4.871496	4.066137	0.257914
C25	1.171606	0.591884	3.317627	C75	-4.731904	3.328175	1.441858
C26	0.657110	-0.695087	3.125090	C76	-4.206976	2.042481	1.401718
C27	1.560391	-1.829453	3.052940	O77	-5.400828	5.315238	0.396458
C28	1.033376	-2.768598	2.079143	C78	-5.558344	6.112655	-0.767006
C29	1.911808	-3.485567	1.259031	H79	-3.475075	-0.417014	1.141764
C30	1.592000	-3.656499	-0.137311	H80	-3.090097	-2.622088	-0.053513
C31	2.824178	-3.561571	-0.903661	H81	-2.854993	-2.521450	-1.812630
C32	2.824648	-2.932072	-2.147612	H82	-5.150583	-1.576651	-2.080109
C33	3.912901	-2.041650	-2.512271	H83	-5.507265	0.004370	-1.392784
C34	3.349242	-0.935632	-3.270070	H84	-5.799713	-1.006806	0.869156
C35	3.853669	0.354842	-3.096358	H85	-5.416278	-2.614886	0.215683
C36	2.944506	1.487290	-3.020387	H86	-7.711124	-3.336112	0.745546
C37	3.477274	2.429636	-2.049229	H87	-8.059592	-1.711803	1.380257
C38	2.609859	3.136484	-1.213597	H88	-9.749711	-1.362852	-0.432252
C39	2.940493	3.312692	0.191849	H89	-9.402263	-2.985417	-1.071743
C40	4.123363	2.775999	0.703675	H90	-11.706353	-3.680202	-0.536941
C41	4.122479	2.120820	2.002029	H91	-12.045551	-2.051346	0.112397
C42	2.937978	2.028658	2.735892	H92	-12.210524	-3.484847	1.165933
C43	2.604995	0.793353	3.427321	H93	-3.640300	1.770381	-1.926558
C44	3.471197	-0.299654	3.355800	H94	-4.580081	4.042705	-1.890792
C45	2.937298	-1.640194	3.172665	H95	-5.046882	3.780679	2.376808
C46	3.847446	-2.373944	2.307257	H96	-4.110237	1.480537	2.328053
C47	3.344036	-3.278910	1.370572	H97	-5.984334	7.057832	-0.425788
C48	3.909997	-3.326682	0.031701	H98	-6.243189	5.645749	-1.487163
C49	4.955177	-2.468144	-0.315257	H99	-4.595242	6.305096	-1.257726
C50	4.956690	-1.812583	-1.613339				

Supplementary information

Synthesis of fulleropyrrolidine derivatives

General Procedure:

Regents and solvents were purchased from common commercial sources and used as received or purified by distillation over appropriate drying agents. Reactions requiring anhydrous conditions were carried out under argon with dry, freshly distilled solvents, and magnetic stirring. Fullerene was supplied by Frontier Carbon Co. Ltd. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on JEOL MH500 spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in $CDCl_3$ as an internal reference. ^{19}F-NMR spectra were recorded on JEOL MH500 spectrometer. Chemical shifts are expressed in ppm downfield from hexafluorobenzene (C_6F_6) in $CDCl_3$ as an internal reference. IR spectra were obtained on SIMAZU FT-IR 8000 spectrometer. MALDI-TOF MS spectra were taken on BRUKER AutoFLEX-T2.



Scheme S1

Benzyl 2-(2-(2-hydroxyethoxy)ethylamino)acetate (S2)

Step 1: A solution of bromoacetic acid (20.8 g, 150 mmol), benzylalcohol (16.2 g, 150 mmol), and p-TsOH (258 mg, 1.5 mmol) in benzene (300 mL) was stirred at 120 ºC for 24 h with continuous water removal using Dean-Stark trap. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (hexane/ethyl acetate=10/1, 5/1), affording bromoacetic acid benzyl ester **S1** (34.3 g, 150 mmol) as yellow oil in 100% yield: R_f 0.71 (hexane/ethyl acetate=4/1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) δ 3.81 (s, 2H), 5.14 (s, 2H), 7.31 (s, 5H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 25.7, 67.8, 128.3, 128.5, 128.5, 134.9, 166.9; IR (neat, cm^{-1}) 2959, 1751, 1458, 1412, 1377, 1167, 972, 750, 698.

Step 2: To a solution of **S1** (13.7 g, 60 mmol) in CH_2Cl_2 (90 mL) was added triethylamine (17

mL, 120 mmol) at 0 ºC under argon. The reaction mixture was stirred for 20 min followed by addition of a solution of 2-(2-aminoethoxy)ethanol (12 mL, 120 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was stirred for 4 h at rt. Then, the organic layer was washed with water (three times), and dried over $MgSO_4$ and filtered, and evaporated, and purified by silica gel flash column chromatography (ethyl acetate /methanol =1/0, 10/1, 5/1) to give benzyl [2-(2-hydroxyethoxy)ethylamino]acetate (**S2**) (12.2 g, 48.0 mmol) as colorless oil in 80 % yield: R_f 0.48 (ethyl acetate/methanol=2/1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) δ 2.83 (t, 2H, *J*= 5.1Hz), 3.50 (s, 2H), 3.52 (t, 2H, *J*= 4.6Hz), 3.58 (t, 2H, *J*= 5.0Hz), 3.65 (t, 2H, *J*= 4.6Hz), 5.11 (s, 2H), 7.28-7.30 (m, 5H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 48.5, 50.3, 61.3, 66.4, 69.8, 72.2, 126.6, 128.2, 128.4, 135.3, 171.8; IR (neat, cm^{-1}) 3412, 2880, 1719, 1638, 1560, 1508, 1458, 1067, 669.

2-(2-(2-methoxyethoxy)ethylamino)acetic acid (S6)

Step 1: To a solution of **S2** (6.58 g, 26 mmol) in CH_2Cl_2 (50 mL) was added triethylamine (4.3 mL, 31 mmol), followed by addition of 4-(N,N-dimethylamino)pyridine (DMAP) (32 mg, 0.26 mmol) at 0 ºC under argon. The reaction mixture was stirred for 20 min followed by addition of a solution of di-*tert*-butyl dicarbonate (6.77 g, 31 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at rt for 4 h. Then, the mixture poured into water, and extracted with diethyl ether (four times). The combined organic layers were dried over $MgSO_4$ and evaporated, purified by silica gel flash column chromatography (hexane/ethyl acetate=3/1, 2.5/1, 2/1) to give benzyl {tert-butoxycarbonyl-[2-(2-hydroxyethoxy)-ethyl]amino}acetate (**S3**) (5.83 g, 16.5 mmol) as colorless oil in 63 % yield: R_f 0.58 (ethyl acetate/methanol=20/1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) δ 1.34 (d, 9H, *J*= 54.5Hz), 2.19 (brs, 1H), 3.38-3.45 (m, 4H), 3.50-3.60 (m, 4H), 3.99 (d, 2H, *J*= 41.3Hz), 5.09 (d, 2H, *J*= 4.1Hz), 7.25-7.30 (m, 5H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 27.8, 28.1, 47.9, 48.2, 49.8, 50.4, 61.2, 66.4, 69.9, 72.1, 80.1, 127.9, 128.1, 135.3, 155.0, 155.2, 169.9, 170.1; IR (neat, cm^{-1}) 3449, 2934, 2872, 1751, 1701, 1458, 1400, 1367, 1252, 1143; Anal. Calcd for $C_{18}H_{27}NO_6$: C, 61.17; H, 7.70; N, 3.96. Found: C, 60.01; H, 7.75; N, 4.13.

Step 2: To a solution of **S3** (5.83 g, 16.5 mmol) in THF (30 mL) was added NaH (1.2 g, 24.8 mmol, 50% in meneral oil) at 0 ºC under argon. The reaction mixture was stirred for 20 min followed by addition of iodomethane (1.6 mL, 24.8 mmol) at 0 ºC. The reaction mixture was stirred for 20 h at rt, then cooled to 0 ºC, and quenched with water. The aqueous layer was extracted with diethyl ether (three times). The combined organic layers were dried over $MgSO_4$, evaporated, purified by silica gel flash column chromatography (hexane/ethyl acetate=5/1, 3/1) to give benzyl {tert-butoxycarbonyl-

[2-(2-methoxyethoxy)ethyl]amino}acetate (**S4**) (3.02 g, 8.21 mmol) as colorless oil in 50 % yield: R_f 0.54 (hexane/ethyl acetate=1/1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) δ 1.34 (d, 9H, *J*= 51.8Hz), 3.28 (d, 3H, *J*= 2.7Hz), 3.37-3.46 (m, 6H), 3.52 (dt, 2H, *J*=5.4Hz, 16.5Hz), 4.02 (d, 2H, *J*= 34.8Hz), 5.09 (d, 2H, *J*= 4.5Hz), 7.24-7.30 (m, 5H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 24.9, 25.2, 44.7, 45.0, 46.7, 47.4, 55.8, 63.3, 67.2, 68.6, 77.0, 125.0, 125.1, 125.4, 132.5, 152.0, 152.3, 166.8, 167.0; IR (neat, cm^{-1}) 2880, 1751, 1701, 1560, 1458, 1400, 1366, 1117, 698, 617; Anal. Calcd for $C_{19}H_{29}NO_6$: C, 62.11; H, 7.96; N, 3.81. Found: C, 62.15; H, 8.16; N, 3.83.

Step 3: To a solution of **S4** (3.02 g, 8.21 mmol) in CH_2Cl_2 (17 mL) was added trifluoroacetic acid (TFA) (9.0 mL). The reaction mixture was stirred for 7 h at rt, then added 10w% aq. Na_2CO_3 (it is important to keep the pH value of the aqueous layer over pH 10). The water layer was extracted with CH_2Cl_2 (five times) and the combined organic layers were dried over $MgSO_4$, evaporated under reduced pressure to give benzyl [2-(2-methoxyethoxy)ethylamino]acetate (**S5**) (2.18 g, 8.19 mmol) as a yellow oil in 100% yield: R_f 0.32 (ethyl acetate/methanol=20/1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) δ 1.99 (br, 1H), 2.83 (t, 2H, *J*= 5.3Hz), 3.38 (s, 3H), 3.50 (s, 2H), 3.54 (t, 2H, *J*= 4.6Hz), 3.60-3.62 (m, 4H), 5.17 (s, 2H), 7.32-7.38 (m, 5H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 48.5, 50.7, 58.8, 66.2, 70.0, 70.4, 71.6, 128.1, 128.3, 135.4, 171.8; IR (neat, cm^{-1}) 3350, 2876, 1736, 1560, 1458, 1117, 1030, 698, 619; Anal. Calcd for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24. Found: C, 62.28; H, 8.20; N, 5.05.

Step 4: To a solution of **S5** (2.19 g, 8.19 mmol) in methanol (27 mL) was added 10w% of Pd on activate charcoal (219 mg) at rt under argon. The reaction mixture was purged with H_2 gas three times and stirred for 7 h at rt under H_2. The reaction mixture was filtered through a pad of Celite and washed with methanol (100mL). The solvent was evaporated under reduced pressure, leaving [2-(2-methoxyethoxy)ethylamino]acetic acid (**S6**) (1.38 g, 7.78 mmol) as yellow oil in 95% yield: ^{1}H NMR (500 MHz, ppm, MeOD, *J*= Hz) δ 3.21 (t, 2H, *J*= 5.1Hz), 3.38 (s, 3H), 3.51 (s, 2H), 3.57 (t, 2H, *J*= 4.4Hz), 3.65 (t, 2H, *J*= 4.6Hz), 3.73 (t, 2H, *J*= 5.1Hz); ^{13}C NMR (125 MHz, ppm, MeOD) δ 48.1, 50.5, 59.2, 67.1, 71.1, 72.9 171.1; IR (neat, cm^{-1}) 3414, 2827, 1751, 1630, 1369, 1111, 1028, 851, 799; Anal. Calcd for $C_7H_{15}NO_4$: C, 47.45; H, 8.53; N, 7.90. Found: C, 46.20; H, 8.49; N, 7.43.

General method for preparing Fulleropyrrolidine:

A solution of C_{60} (500 mg, 0.694 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid (**S6**) (185 mg, 1.04 mmol), and aldehyde (2.08 mmol) in chlorobenzene (200 mL) was stirred for 0.5 h at 130 ºC under argon. The solvent was evaporated under reduced pressure and the

residue purified by flash chromatography (CS_2/AcOEt=1/0, 20/1, 2/1), affording product **1** as dark brown solid.

N-Methoxyethoxyethyl fulleropyrrolidine (2):

^{1}H NMR (500MHz,$CDCl_3$, J= Hz) δ 3.31-3.39 (2H, m), 3.40 (3H, s), 3.60-3.64 (2H, m), 3.76-3.80 (2H, m), 3.99-4.04 (2H, m), 4.48 (4H, s); ^{13}C NMR (125MHz,$CDCl_3$) δ 54.09, 58.83, 68.26, 70.48, 71.91, 136.00, 139.90, 141.62, 141.80, 141.96, 142.35, 142.84, 144.29, 144.99, 145.16, 145.40, 145.77, 145.81, 145.95, 146.98, 154.76; IR (KBr, cm^{-1}) 2864, 2807, 2778, 1506, 1462, 1427, 1339, 1184, 1107, 768, 575; MALDI-TOF-MS (matrix: SA) found 865.1109 (calcd for $C_{67}H_{15}NO_2^+$, exact mass: 865.1103).

N-Methoxyethoxyethyl-2-phenyl fulleropyrrolidine (1a):

^{1}H NMR (500MHz, $CDCl_3$, J= Hz) δ 2.83 -2.88 (1H, m), 3.38-3.45 (4H, m), 3.60-3.65 (2H, m), 3.71-3.78 (2H, m), 3.93-4.04 (2H,m), 4.28 (1H, d, J= 9.6 Hz), 5.13 (1H, s), 5.19 (1H, d, J= 9.7 Hz), 7.27-7.38 (3H, m), 7.76 (2H, brs); ^{13}C NMR (125MHz, $CDCl_3$) δ 52.02, 58.92, 67.54, 68.97, 70.45, 70.47, 71.95, 76.03, 82.25, 128.33, 128.33, 128.52, 129.26, 135.50, 135.69, 136.36, 136.63, 136.89, 139.21, 139.66, 139.92, 139.98, 141.30, 141.46, 141.59, 141.68, 141.76, 141.81, 141.88, 141.91, 141.94, 142.07, 142.33, 142.46, 142.78, 142.93, 144.15, 144.19, 144.39, 144.50, 144.90, 144.98, 145.02, 145.08, 145.13, 145.30, 145.34, 145.53, 145.70, 145.86, 145.89, 145.94, 145.98, 146.03, 146.07, 146.27, 146.57, 147.05, 153.22, 153.99, 156.27; IR (KBr, cm^{-1}) 2864, 2781, 1452, 1424, 1296, 1180, 1113, 1026, 962, 903, 802, 725, 706, 573; MALDI-TOF-MS (matrix: SA) found 941.1421 (calcd for $C_{73}H_{20}NO_2^+$, exact mass: 941.1416).

N-Methoxyethoxyethyl-2-(2-methylphenyl) fulleropyrrolidine (1b):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.56 (3H, s), 2.80-2.85 (1H, m), 3.32-3.41 (4H, m), 3.59-3.65 (2H, m), 3.71-3.78 (2H, m), 4.33 (1H, d, J= 9.6Hz), 5.18 (1H, d, 9.7Hz), 5.51 (1H, s), 7.16 (2H, d, J= 3.7Hz), 7.23-7.27 (1H, m), 8.05 (1H, d, J= 7.8Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 20.54, 51.76, 58.94, 67.36, 69.38, 70.47, 70.49, 71.99, 75.99, 126.48, 127.78, 129.75, 130.84, 135.05, 135.24, 135.61, 136.41, 136.66, 137.14, 139.32, 139.68, 139.97, 140.13, 141.37, 141.50, 141.63, 141.71, 141.85, 141.95, 142.04, 142.11, 142.15, 142.43, 142.49, 142.82, 142.97, 144.17, 144.23, 144.47, 144.99, 145.11, 145.17, 145.23, 145.30, 145.34, 145.39, 145.58, 145.75, 145.92, 145.99, 146.07, 146.11, 146.15, 146.48, 147.11, 153.57, 153.74, 154.04, 156.66; IR (KBr, cm^{-1}) 3443, 2909, 2866, 2808, 1460, 1427, 1285, 1180, 1105, 1045, 1030, 903, 729, 573; MALDI-TOF-MS (matrix: SA) found 955.1576

(calcd for $C_{74}H_{21}NO_2$ exact mass: 955.1572)

N-Methoxyethoxyethyl-2-(3-methylphenyl) fulleropyrrolidine (1c):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.35, (3H, s), 2.82-2.87 (1H, m), 3.39-3.45 (4H, m), 3.60-3.66 (2H, m), 3.72-3.79 (2H, m), 3.93-4.04 (2H, m), 4.27 (1H, d, J= 9.6Hz), 5.09 (1H, s), 5.19 (1H, d, J= 9.6Hz), 7.09 (1H, d, J= 7.3Hz), 7.19- 7.27 (1H, m), 7.55 (2H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 21.55, 52.08, 58.92, 67.61, 69.03, 70.49, 71.99, 76.08, 82.36, 126.43, 128.48, 129.14, 135.52, 135.66, 136.43, 136.59, 136.82, 137.91, 139.27, 139.69, 139.95, 140.02, 141.35, 141.50, 141.62, 141.74, 141.85, 141.92, 141.96, 142.10, 142.38, 142.49, 142.81, 142.97, 144.20, 144.46, 144.54, 144.94, 145.03, 145.06, 145.10, 145.16, 145.36, 145.59, 145.74, 145.89, 145.93, 145.97, 146.03, 146.06, 146.12, 146.32, 146.67, 147.09, 153.39, 154.12, 156.35; IR (KBr, cm^{-1}) 2857, 2781, 1734, 1605, 1460, 1427, 1182, 1107, 1092, 907, 708, 729, 708; MALDI-TOF-MS (matrix: SA) found 955.1572 (calcd for $C_{74}H_{21}NO_2^+$ exact mass: 955.1572)

N-Methoxyethoxyethyl-2-(4-methylphenyl) fulleropyrrolidine (1d):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.33 (3H, s), 2.79-2.84 (1H, m), 3.37-3.43 (4H, m), 3.57-3.64 (2H, m), 3.67-3.77 (2H, m), 3.90-4.02 (1H, m), 4.25 (1H, d, J= 9.6Hz), 5.08 (1H, s), 5.18 (1H, d, J= 9.7Hz), 7.15 (2H, d, J= 8.3Hz), 7.62 (2H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 21.27, 52.01, 58.79, 67.53, 68.89, 70.46, 70.51, 71.96, 76.05, 82.08, 129.15, 129.24, 133.79, 135.44, 135.57, 136.32, 136.57, 137.81, 139.21, 139.64, 139.86, 139.93, 141.27, 141.41, 141.52, 141.52, 141.65, 141.72, 141.75, 141.82, 141.86, 141.89, 142.00, 142.28, 142.39, 142.72, 142.87, 144.10, 144.36, 144.44, 144.84, 144.91, 144.96, 145.01, 145.08, 145.23, 145.29, 145.50, 145.64, 145.79, 145.83, 145.88, 145.92, 145.97, 146.02, 146.08, 146.23, 146.57, 146.98, 153.31, 153.34, 153.99, 156.28; IR (KBr, cm^{-1}) 2907, 2864, 2807, 1508, 1458, 1424, 1339, 1304, 1179, 1107, 822, 770, 573; MALDI-TOF-MS (matrix: SA) found 955.1575 (calcd for $C_{74}H_{21}NO_2^+$ exact mass: 955.1572)

N-Methoxyethoxyethyl-2-(2-chlorophenyl)fulleropyrrolidine (1e):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.87-2.90 (1H, m), 3.30-3.34 (1H, m), 3.41 (3H, s), 3.62-3.64 (2H, m), 3.71-3.78 (2H, m), 3.92-4.00 (2H, m), 4.38 (1H, d, J= 9.6Hz), 5.18 (1H, d, J= 9.6Hz), 7.21-7.25 (1H, m), 7.34-7.38 (2H, m), 8.14 (1H, dd, J= 2.5Hz, 1.9Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 51.84, 58.93, 67.12, 69.24, 70.22, 70.54, 71.99, 75.41, 76.66, 127.15, 128.08, 128.86, 129.13, 129.93, 131.35, 134.84, 135.02, 135.12, 135.84, 135.84, 136.59, 139.31, 139.58, 140.01, 140.05, 141.46, 141.56, 141.78, 141.84, 141.95, 142.00,

142.04, 142.14, 142.39, 142.45, 142.81, 142.89, 144.19, 144.22, 144.37, 144.41, 144.93, 145.00, 145.10, 145.16, 145.23, 145.28, 145.36, 145.38, 145.47, 145.70, 145.78, 145.87, 145.95, 146.02, 146.06, 146.37, 147.10, 153.08, 153.60, 153.76, 156.47; IR (KBr, cm^{-1}) 2909, 2864, 2808, 1462, 1429, 1180, 1109, 1034, 754; MALDI-TOF-MS (matrix: SA) found 975.1029 (calcd for $C_{73}H_{18}ClNO_2^+$ exact mass: 975.1026).

N-Methoxyethoxyethyl-2-(3-chlorophenyl)fulleropyrrolidine (1f):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.85-2.90 (1H, m), 3.37-3.41 (4H, m), 3.60-3.65 (2H, m), 3.72-3.79 (2H, m), 3.92-4.04 (2H, m), 4.28 (1H, d, J= 9.7Hz), 5.12 (1H, s), 5.19 (1H, d, J= 9.7Hz), 7.25-7.33 (2H, m), 7.67 (1H, br), 7.78 (1H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.07, 58.85, 67.40, 68.86, 70.24, 70.51, 71.94, 75.70, 81.46, 127.34, 128.04, 128.51, 128.81, 129.71, 135.38, 136.25, 136.74, 139.24, 139.30, 139.75, 139.97, 140.00, 141.34, 141.45, 141.60, 141.63, 141.74, 141.78, 141.85, 141.90, 142.02, 142.34, 142.46, 142.78, 142.91, 144.10, 144.17, 144.36, 144.49, 144.91, 144.97, 145.03, 145.09, 145.13, 145.18, 145.24, 145.33, 145.36, 145.49, 145.58, 145.70, 145.85, 145.89, 145.94, 146.03, 146.07, 146.12, 146.27, 147.05, 152.45, 152.73, 153.73, 155.94; IR (KBr, cm^{-1}) 2907, 2857, 2807, 1462, 1429, 1136, 1107, 1076, 768; MALDI-TOF-MS (matrix: SA) found 975.1020 (calcd for $C_{73}H_{18}ClNO_2$ exact mass: 975.1026).

N-Methoxyethoxyethyl-2-(4-chlorophenyl)fulleropyrrolidine (1g):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.84-2.89 (1H, m), 3.42 (3H, s), 3.42-3.49 (1H, m), 3.60-3.67 (2H, m), 3.70-3.80 (3H, m), 3.93-4.30 (2H, m), 5.13 (1H, s), 5.20 (1H, d, J= 9.6 Hz), 7.36 (2H, d, J= 8.7 Hz), 7.74-7.75 (2H, m); ^{13}C NMR (100 MHz, ppm, $CDCl_3$) δ 52.02, 58.98, 67.51, 68.94, 70.34, 70.53, 71.98, 75.90, 76.67, 77.00, 77.31, 81.52, 128.83, 130.58, 134.26, 135.48, 135.63, 135.79, 136.30, 136.83, 139.43, 139.81, 140.04, 140.07, 141.42, 141.55, 141.70, 141.83, 141.88, 141.93, 141.98, 142.01, 142.11, 142.42, 142.55, 142.87, 143.01, 144.20, 144.26, 144.45, 144.56, 145.01, 145.05, 145.10, 145.14, 145.19, 145.29, 145.33, 145.40, 145.56, 145.81, 145.94, 145.99, 146.03, 146.06, 146.12, 146.24, 146.39, 147.14, 152.71, 152.94, 153.84, 156.13; IR (KBr, cm^{-1})
2862, 2802, 1560, 1541, 1508, 1489, 1458, 1419, 1338, 1180, 1107, 1089, 1014, 839, 829,597,572,526;; MALDI-TOF-MS (matrix: SA) found 975.1024 (calcd for $C_{74}H_{20}ClNO_2$, exact mass: 977.1518)

N-Methoxyethoxyethyl-2-(2-bromophenyl) fulleropyrrolidine (1h):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.90 (1H, quin, J= 62Hz), 3.29-3.34 (1H, m), 3.41

(3H, s), 3.63 (2H, t, J= 4.6Hz), 3.72-3.80 (2H, m), 3.92-4.01 (2H, m), 4.40 (1H, d, J= 9.7Hz), 5.18 (1H, d, J= 9.6Hz), 5.82 (1H, s), 7.16 (1H, t, J= 7.3Hz), 7.42 (1H, t, J= 7.6Hz), 7.57 (1H, d, J= 8.2Hz), 8.14 (1H, d, J= 7.8Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) (125 MHz, ppm, CDCl3) δ 51.77, 58.86, 67.00, 69.17, 70.19, 70.51, 71.95, 75.40, 78.95, 125.70, 127.65, 129.45, 131.69, 133.20, 134.94, 135.84, 136.17, 136.29, 136.54, 139.24, 139.52, 140.00, 141.39, 141.47, 141.54, 141.72, 141.78, 141.87, 141.98, 142.09, 142.31, 142.34, 142.39, 142.77, 142.84, 144.13, 144.17, 144.32, 144.35, 144.87, 144.94, 145.04, 145.12, 145.20, 145.22, 145.29, 145.34, 145.41, 145.63, 145.71, 145.84, 145.89, 145.97, 146.00, 146.32, 146.40, 147.03, 152.97, 153.54, 153.73, 156.44; IR (KBr, cm^{-1}) 2911, 2866, 2810, 1458, 1429, 1182, 1109, 1024, 870, 847, 754, 669; MALDI-TOF-MS (matrix: SA) found 1019.0522 (calcd for $C_{73}H_{18}BrNO_2$ exact mass: 1019.0521)

N-Methoxyethoxyethyl-2-(3-bromophenyl) fulleropyrrolidine (1i):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.84-2.89 (1H, m), 3.36-3.41 (4H, m), 3.60-3.63 (2H, m), 3.72-3.77 (2H, m), 3.92-4.04 (2H, m), 4.28 (1H, d, J= 9.6Hz), 5.10 (1H, s), 5.19 (1H, d, J= 9.6Hz), 7.26 (1H, t, J= 8.0Hz), 7.42, (1H, ddd, J= 8.0Hz, 2.0Hz, 1.1Hz), 7.72 (1H, br), 7.93 (1H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.06, 58.85, 67.39, 68.84, 70.22, 70.51, 71.94, 75.72, 81.38, 127.78, 128.03, 128.81, 129.98, 131.43, 135.74, 136.24, 136.73, 139.30, 139.48, 139.96, 140.00, 141.34, 141.45, 141.60, 141.62, 141.74, 141.78, 141.79, 141.85, 141.89, 141.92, 142.01, 142.33, 142.36, 142.46, 142.91, 144.10, 144.17, 144.36, 144.48, 144.91, 144.96, 145.00, 145.03, 145.08, 145.12, 145.16, 145.23, 145.32, 145.36, 145.49, 145.57, 145.70, 145.84, 145.88, 145.94, 145.96, 146.03, 146.07, 147.04, 152.71, 153.70, 155.92; IR (KBr, cm^{-1}) 2916, 2866, 2807, 1560, 1541, 1508, 1458, 1425, 1180, 1109, 1070; MALDI-TOF-MS (matrix: SA) found 1019.0519 (calcd for 18$BrNO_2$ exact mass: 1019.0521)

N-Methoxyethoxyethyl-2-(4-bromophenyl) fulleropyrrolidine (1j):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.83-2.88 (1H, m), 3.35-3.42 (4H, m), 3.58-3.65 (2H, m), 3.71-3.78 (2H, m), 3.91-3.95 (1H, m), 3.99-4.03 (1H, m), 4.28 (1H, d, J= 9.6Hz), 5.11 (1H, s), 5.20 (1H, d, J= 9.7Hz), 7.50 (2H, d, 8.7Hz), 7.67 (2H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.09, 58.87, 67.50, 68.88, 70.35, 70.54, 71.99, 75.78, 81.55, 122.68, 131.73, 135.41, 136.08, 136.24, 136.78, 139.41, 139.79, 140.00, 140.04, 141.37, 141.49, 141.65, 141.78, 141.83, 141.88, 141.92, 141.96, 142.05, 142.39, 142.42, 142.50, 142.81, 142.96, 144.14, 144.20, 144.41, 144.51, 144.95, 145.00, 145.04, 145.09, 145.13, 145.26, 145.36, 145.50, 145.74, 145.90, 145.94, 145.98, 146.07, 146.11, 146.17, 146.32, 147.09, 152.59, 152.85, 153.76, 156.04; IR (KBr, cm^{-1}) 2862, 2802, 1560, 1541, 1508, 1489, 1458, 1419,

1180, 1107, 1089, 1014, 829, 597, 572; MALDI-TOF-MS (matrix: SA) found 1019.0530 (calcd for $C_{73}H_{18}BrNO_2$ exact mass: 1019.0521)

N-Methoxyethoxyethyl-2-(2-fluorophenyl) fulleropyrrolidine (1k):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.87-2.91 (1H, m), 3.36-3.41 (4H, m), 3.62-3.64 (2H, m), 3.72-3.79 (2H, m), 3.93-4.03 (2H, m), 4.34 (1H, d, J= 9.7Hz), 5.19 (1H, d, J= 9.6Hz), 7.05-7.28 (4H, m), 8.03 (1H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 51.95, 58.93, 67.27, 69.06, 70.22, 70.52, 71.96, 73.27, 75.31, 115.57, 115.74, 124.53, 129.51, 130.57, 135.39, 135.71, 139.29, 139.73, 140.00, 141.45, 141.49, 141.53, 141.78, 141.91, 141.96, 142.04, 142.11, 142.35, 142.42, 142.45, 142.80, 142.88, 144.19, 144.36, 144.45, 144.90, 144.97, 145.02, 145.09, 145.15, 145.26, 145.27, 145.34, 145.36, 145.47, 145.74, 145.87, 145.95, 146.00, 146.05, 146.16, 146.29, 146.29, 147.08, 153.02, 153.39, 153.62, 156.27; ^{19}F NMR (470 MHz, ppm, $CDCl_3$) δ 46.38 (1F, s); IR (KBr, cm^{-1}) 2862, 2802, 1560, 1541, 1508, 1489, 1458, 1419, 1180, 1107, 1089, 1014, 829, 597, 572; MALDI-TOF-MS (matrix: SA) found 959.1319 (calcd for $C_{73}H_{18}FNO_2^+$ exact mass: 959.1322)

N-Methoxyethoxyethyl-2-(3-fluorophenyl) fulleropyrrolidine (1l):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.85-2.90 (1H, m), 3.38-3.44 (4H, m), 3.60-3.65 (2H, m), 3.72-3.79 (2H, m), 3.93-4.04 (2H, m), 4.28 (1H, d, J= 9.6Hz), 5.15 (1H, s), 5.19 (1H, d, J= 9.7Hz), 6.96-7.00 (1H, m), 7.32-7.53 (3H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.08, 58.84, 67.39, 68.85, 70.25, 70.50, 71.92, 75.69, 81.45, 115.36, 124.87, 129.98, 135.37, 135.72, 136.24, 136.67, 139.24, 139.68, 139.94, 139.98, 141.30, 141.43, 141.56, 141.63, 141.72, 141.76, 141.78, 141.83, 141.88, 141.91, 142.00, 142.32, 142.34, 142.43, 142.76, 142.89, 144.08, 144.15, 144.34, 144.46, 144.89, 144.95, 144.99, 145.05, 145.10, 145.17, 145.23, 145.32, 145.47, 145.61, 145.68, 145.83, 145.86, 145.94, 146.01, 146.05, 146.34, 147.03, 152.57, 152.76, 153.74, 155.94; ^{19}F NMR (470 MHz, ppm, $CDCl_3$) δ 51.08 (1F, s); IR (KBr, cm^{-1}) 2909, 2864, 2807, 1589, 1449, 1425, 1265, 1252, 1108, 1134, 1107, 770, 575; MALDI-TOF-MS (matrix: SA) found 959.1321 (calcd for $C_{73}H_{18}FNO_2$ exact mass: 959.1322)

N-Methoxyethoxyethyl-2-(4-fluoromethylphenyl) fulleropyrrolidine (1m):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.82-2.85 (1H, m), 3.37 (3H, s), 3.59-3.61 (2H, m), 3.71-3.74 (2H, m), 3.92-3.94 (1H, m), 3.97-4.00 (1H, m), 4.27 (1H, d, J= 19.0 Hz), 5.19 (1H, s), 5.20 (1H, d, J= 19.0 Hz), 7.04 (2H, t, J= 17.0 Hz), 7.75 (2H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.01, 59.19, 67.63, 69.11, 70.41, 70.59, 72.07, 76.21, 81.62, 115.59, 115.74, 131.03, 131.09, 132.98, 135.63, 135.90, 136.45, 136.91, 139.47, 139.90, 140.14,

140.19, 141.53, 141.68, 141.82, 141.87, 141.98, 142.02, 142.05, 142.10, 142.13, 142.17, 142.27, 142.55, 142.57, 142.69, 143.00, 143.17, 144.36, 144.42, 144.59, 144.72, 145.15, 145.21, 145.26, 145.33, 145.52, 145.72, 145.94, 145.95, 146.04, 146.11, 146.14, 146.17, 146.21, 146.28, 146.30, 146.46, 146.61 147.32, 153.16, 153.29, 154.13, 156.47, 161.72; ^{19}F NMR (470 MHz, ppm, $CDCl_3$) δ 49.55 (1F, s); IR (KBr, cm^{-1}) 2880, 1508, 1225, 1109, 754, 527; MALDI-TOF-MS (matrix: SA) found 959.1323 (calcd for $C_{73}H_{18}FNO_2$ exact mass: 959.1322)

N-Methoxyethoxyethyl-2-(2-trifluoromethylphenyl) fulleropyrrolidine (1n):
^{1}H NMR (400 MHz, ppm, $CDCl_3$, J= Hz) δ 2.86-2.91 (1H, m), 3.19-3.24 (1H, m), 3.43 (3H, s), 3.61-3.67 (2H, m), 3.71-3.79 (2H, m), 3.90-3.99 (2H, m), 4.32 (1H, d, J= 9.5 Hz), 5.19 (1H, d, J= 9.5 Hz), 5.60 (1H, s), 7.44 (1H, t, J= 7.5 Hz), 7.65 (1H, t, J= 7.5Hz), 7.74 (1H, d, J= 8.0 Hz), 8.53 (1H, d, J= 7.5Hz); ^{13}C NMR (100 MHz, ppm, $CDCl_3$) δ 51.79, 59.11, 67.21, 69.51, 70.31, 70.48, 71.93, 75.76, 76.88, 125.81, 125.86, 128.54, 131.92, 132.71, 135.09, 135.83, 136.12, 136.33, 136.95, 139.37, 139.54, 140.10, 140.17, 141.50, 141.58, 141.66, 141.90, 141.92, 142.02, 142.04, 142.10, 142.14, 142.27, 142.48, 142.56, 142.96, 143.06, 144.32, 144.39, 144.59, 145.03, 145.10, 145.25, 145.28, 145.47, 145.52, 145.55, 145.90, 145.97, 146.08, 146.14, 146.17, 146.36, 147.22, 147.26, 153.16, 153.58, 153.86, 153.86, 156.50; ^{19}F NMR (470 MHz, , ppm, $CDCl_3$) δ 55.51 (3F, s); IR (KBr, cm^{-1}) 2920, 2868, 2814, 1449, 1429, 1307, 1161, 1123, 1061, 1034, 770, 527.

N-Methoxyethoxyethyl-2-(4-trifluoromethylphenyl) fulleropyrrolidine (1o): (400 MHz, ppm, CDCl3, J= Hz) δ 2.84-2.90 (1H, m), 3.32-3.42 (1H, m), 3.39 (1H, s), 3.56-3.65 (2H, m), 3.70-3.78 (2H, m), 3.91-3.95 (1H, m), 3.99-4.04 (1H, m), 4.31 (1H, d, J= 9.8Hz), 5.21 (1H, s), 5.22 (1H, d, J= 9.8Hz), 7.63 (2H, d, J= 7.8Hz), 7.93 (2H, d, J= 6.9Hz); ^{13}C NMR (100 MHz, ppm, $CDCl_3$) δ 52.25, 58.77, 67.60, 68.56, 70.41, 70.51, 71.87, 75.82, 77.68, 126.37, 126.44, 127.83, 127.99, 128.76, 135.27, 135.60, 136.33, 136.74, 139.28, 139.60, 139.84, 139.89, 140.72, 141.28, 141.36, 141.56, 141.66, 141.71, 141.73, 141.81, 141.83, 141.85, 141.92, 141.94, 142,27, 142.37, 142.68, 142.68, 142.83, 144.03, 144.06, 144.32, 144.40, 144.81, 144.89, 144.91, 144.95, 145.01, 145.05, 145.11, 145.17, 145.24, 145.29, 145.45, 145.61, 145.75, 145.78, 145.84, 145.88, 145.96, 146.00, 146.02, 146.55, 146.96, 152.82, 152.96, 153.77, 155.82;; ^{19}F NMR (470 MHz, ppm, $CDCl_3$) δ 98.81 (3F, s); IR (KBr, cm^{-1}) 2903, 2864, 2807, 1424, 1321, 1163, 1121, 1108, 1067, 1018, 867, 802, 527.

N-Methoxyethoxyethyl-2-(3-methoxyphenyl) fulleropyrrolidine (1q):

Supplementary information

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.77-2.84 (1H, m), 3.88 (3H, s), 3.59-3.61 (2H, m), 3.69-3.75 (3H, m), 3.75-3.79 (3H, s), 3.81-4.01 (2H, m), 4.24 (1H, d, J= 12.2 Hz), 5.06 (1H, s), 5.17 (1H, d, 12.2 Hz), 6.86 (2H, d, J= 10.4 Hz), 7.63-7.65 (2H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 51.99 ,54.62, 58.74, 67.49, 68.77, 70.47, 70.52, 71.95, 76.14, 76.69, 77.00, 77.33, 81.76, 113.84, 128.01, 128.62, 130.23, 135.41, 135.53, 136.28, 136.53, 139.25, 139.66, 139.84, 139.00, 141.24, 141.37, 141.52, 141.63, 141.68, 141.80, 141.83, 141.86, 141.99, 142.26, 142.29, 142.37, 142.70, 142.85, 144.07, 144.35, 144.41, 144.81, 144.89, 144.99, 145.05, 145.19, 145.27, 145.47, 145.60, 145.76, 145.80, 145.84, 145.94, 145.99, 146.07, 146.21, 146.50, 146.96, 153.30, 153.35, 153.94, 156.28, 159.27; IR (Neat, cm^{-1}) ; 2864, 2826, 1597, 1584, 1560, 1483, 1458, 1425, 1283, 1265, 1179, 1107, 1042, 903, 872, 770, 727, 708, 692, 598, 575: MALDI-TOF-MS (matrix: SA) found 971.1547 (calcd for $C_{74}H_{21}NO_3^+$, exact Mass: 971.1522).

N-Methoxyethoxyethyl-2-(4-methoxyphenyl)fulleropyrrolidine (1r)

^{1}H NMR (400 MHz, ppm, $CDCl_3$, J= Hz) δ 2.77-2.84 (1H, m), 3.88 (3H, s), 3.59-3.61 (2H, m), 3.69-3.75 (3H, m), 3.75-3.79 (3H, s), 3.81-4.01 (2H, m), 4.24 (1H, d, J= 12.2 Hz), 5.06 (1H, s), 5.17 (1H, d, 12.2 Hz), 6.86 (2H, d, J= 10.4 Hz), 7.63-7.65 (2H, m); ^{13}C NMR (100 MHz, ppm, $CDCl_3$) δ 51.99 ,54.62, 58.74, 67.49, 68.77, 70.47, 70.52, 71.95, 76.14, 76.69, 77.00, 77.33, 81.76, 113.84, 128.01, 128.62, 130.23, 135.41, 135.53, 136.28, 136.53, 139.25, 139.66, 139.84, 139.00, 141.24, 141.37, 141.52, 141.63, 141.68, 141.80, 141.83, 141.86, 141.99, 142.26, 142.29, 142.37, 142.70, 142.85, 144.07, 144.35, 144.41, 144.81, 144.89, 144.99, 145.05, 145.19, 145.27, 145.47, 145.60, 145.76, 145.80, 145.84, 145.94, 145.99, 146.07, 146.21, 146.50, 146.96, 153.30, 153.35, 153.94, 156.28, 159.27; IR (KBr, cm^{-1}) 3460, 2943, 2893, 2866, 2827, 1608, 1508, 1456, 1429, 1301, 1246, 1180, 1170, 1107, 1033, 831, 572, 526; MALDI-TOF-MS (matrix: SA) found 971.1522 (calcd for $C_{74}H_{21}NO_3^+$, exact Mass: 971.1522).

N-Methoxyethoxyethyl-2-(2,6-dimethoxyphenyl) fulleropyrrolidine (1s):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.81-2.87 (1H, m), 3.99 (3H, s), 3.44-3.49 (1H, m), 3.59-3.61 (2H, m), 3.71 (9H, s), 3.93-4.25 (2H, m), 4.25 (1H, d, J= 9.7 Hz), 5.02 (1H, s), 5.17 (1H, d, 9.6 Hz), 6.98-7.28 (2H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 51.80, 55.02, 55.90, 59.11, 67.35, 70.07, 70.26, 70.34, 71.95, 72.02, 73.82, 75.31, 104.13, 105.01, 112.40, 129.90, 134.39, 135.88, 136.63, 136.86, 139.01, 139.63, 139.84, 139.87, 141.26, 141.54, 141.56, 141.69, 141.91, 141.94, 141.98, 142.00, 142.18, 142.24, 142.26, 142.35, 142.42, 142.45, 142.48, 142.94, 143.01, 144.31, 144.36, 144.57, 144.59, 144.83, 144.94, 145.03,

145.11, 145.13, 145.16, 145.39, 145.55, 145.71, 145.75, 145.80, 145.82, 145.84, 145.87, 145.98, 145.98, 146.03, 146.07, 146.16, 146.17, 146.61, 146.67, 147.10, 147.17, 154.86, 154.95, 155.57, 157.13, 159.83, 159.88; IR (KBr, cm^{-1}) 2924, 2862, 2828, 1591, 1474, 1460, 1429, 1252, 1109, 774, 527.

N-Methoxyethoxyethyl-2-(3,4,5-trimethoxyphenyl) fulleropyrrolidine (1t):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.81-2.87 (1H, m), 3.99 (3H, s), 3.44-3.49 (1H, m), 3.59-3.61 (2H, m), 3.71 (9H, s), 3.93-4.25 (2H, m), 4.25 (1H, d, J= 9.7 Hz), 5.02 (1H, s), 5.17 (1H, d, 9.6 Hz), 6.98-7.28 (2H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.23, 55.80, 58.74, 60.27, 67.42, 68.77, 70.41, 70.54, 70.57, 71.98, 75.89, 76.75, 77.00, 77.25, 82.24, 132.16, 135.53, 135.98, 136.26, 139.42, 139.50, 139.85, 139.98, 141.33, 141.40, 141.53, 141.57, 141.75, 141.81, 141.89, 141.95, 142.29, 142.33, 142.36, 142.43, 142.73, 142.93, 144.07, 144.12, 144.42, 144.86, 144.98, 145.10, 145.19, 145.23, 145.29, 145.44, 145.65, 145.70, 145.80, 145.84, 145.93, 145.97, 146.04, 146.11, 146.61, 147.00, 153.12, 153.12, 153.54, 153.88, 155.95; IR (KBr, cm^{-1}) 2926, 2868, 2827, 1232, 1182, 1122, 1003, 848, 669, 526, 418; MALDI-TOF-MS (matrix: non) found 1031.1767 (calcd for $C_{76}H_{25}NO_5^+$ exact mass: 1031.1733)

N-Methoxyethoxyethyl-2-(2-hexyloxyphenyl)fulleropyrrolidine (1u):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 0.89 (3H, t, J= 6.7Hz), 1.29-1.32 (5H, m), 1.43 (2H, quin, 7.3Hz), 1.73 (2H, quin, 7.2Hz), 2.84-2.87 (1H, m), 3.37-3.47 (4H, m), 3.61-3.63 (2H, m), 3.74-3.77 (2H, m), 3.90-4.02 (4H, m), 4.27 (1H, d, J= 9.7Hz), 5.08 (1H, s), 5.19 (1H, d, J= 9.7Hz), 6.78 (1H, dd, J= 9.2Hz, 2.8Hz), 7.22-7.26 (3H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 14.15, 22.78, 29.25, 31.68, 52.10, 58.87, 67.56, 67.79, 68.98, 70.49, 71.98, 75.94, 82.23, 135.47, 135.62, 136.44, 138.34, 139.30, 139.63, 139.91, 140.00, 141.35, 141.46, 141.60, 141.69, 141.79, 141.85, 141.89, 142.03, 142.36, 142.46, 142.78, 142.94, 144.16, 144.43, 144.50, 144.91, 144.99, 145.31, 145.55, 145.71, 145.85, 145.94, 146.09, 146.26, 146.71, 147.06, 153.29, 153.37, 154.05, 156.23; IR (KBr, cm^{-1}) 2920, 2853, 1597, 1583, 1456, 1429, 1287, 1265, 1231, 1182, 1109, 770, 669; MALDI-TOF-MS (matrix: SA) found 1041.2300 (calcd for $C_{79}H_{31}NO_3^+$, exact mass: 1041.2304)

N-Methoxyethoxyethyl-2-(3-hexyloxyphenyl)fulleropyrrolidine (1v):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 0.88 (3H, t, J= 71Hz), 1.29-1.31 (5H, m), 1.42 (2H, quin, J= 7.3Hz), 1.72 (2H, quin, J= 7.0Hz), 2.75-2.79 (1H, m), 3.30-3.38 (4H, m), 3.55-3.57 (2H, m), 3.67-3.70 (2H, m), 3.84-3.89 (3H, m), 3.93-3.97 (1H, m), 4.21 (1H, d, J=

9.6Hz), 5.02 (1H, s), 5.16 (1H, d, J= 9.6Hz), 6.80 (2H, d, J= 8.7Hz), 7.58 (2H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 14.19, 22.88, 25.87, 29.36, 31.69, 52.02, 58.56, 67.41, 67.44, 68.68, 70.42, 70.52, 71.93, 76.08, 81.69, 128.22, 130.08, 135.33, 135.42, 136.21, 136.44, 139.17, 139.56, 141.16, 141.28, 141.43, 141.55, 141.60, 141.70, 141.74, 141.89, 142.16, 144.27, 144.32, 144.71, 144.80, 144.87, 144.97, 145.10, 145.18, 145.38, 145.51, 145.71, 145.75, 145.84, 145.90, 146.02, 146.13, 146.43, 146.86, 153.26, 153.89, 156.22, 158.82; IR (KBr, cm^{-1}) 2918, 2853, 1609, 1508, 1462, 1423, 1423, 1300, 1244, 1171, 1107, 1026, 839, 802; MALDI-TOF-MS (matrix: SA) found 1041.2297 (calcd for $C_{79}H_{31}NO_3$, exact mass: 1041.2304)

N-Methoxyethoxyethyl-2-(4-hexyloxyphenyl)fulleropyrrolidine (1w):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 0.85-0.88 (3H, m), 1.24-1.39 (15H, m), 1.58-1.64 (2H, m), 2.84-2.86 (1H, m), 3.44-3.49 (4H, m), 3.65-3.81 (5H, m), 3.97-4.05 (3H, m), 4.33 (1H, d, J= 9.6Hz), 5.19 (1H, d, 9.2Hz), 5.77 (1H, s), 6.88 (1H, 7.8Hz), 7.03 (1H, t, J= 7.3Hz), 7.21-7.23 (1H, m), 7.99 (1H, dd, J= 7.6Hz, 1.1Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 14.17, 22.68, 25.98, 29.11, 29.42, 31.82, 52.14, 59.11, 67.47, 67.96, 69.39, 70.47, 70.51, 71.99, 74.29, 75.51, 111.44, 120.78, 125.47, 128.90, 129.85, 135.95, 139.98, 140.05, 141.58, 141.60, 141.72, 141.86, 141.95, 141.98, 142.04, 142.19, 142.41, 142.44, 142.51, 142.88, 144.26, 144.33, 144.47, 144.97, 145.12, 145.51, 145.61, 145.78, 145.82, 145.93, 145.97, 146.04, 146.10, 146.74, 147.17, 154.06, 154.31, 155.41, 157.63; IR (KBr, cm^{-1}) 2920, 2851, 1599, 1585, 1558, 1539, 1489, 1454, 1429, 1285, 1242, 1180, 1107, 1045, 752, 575; MALDI-TOF-MS (matrix: SA) found 1069.2616 (calcd for $C_{81}H_{35}NO_3^+$, exact mass: 1069.2617)

N-Methoxyethoxyethyl-2-(2-naphthyl)fulleropyrrolidine (1x):

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.87-2.92 (1H, m), 3.38-3.45 (4H, m), 3.61-3.63 (2H, m), 3.72-3.76 (2H, m), 3.93-4.08 (2H, m), 4.34 (1H, d, J=9.6 Hz), 5.25 (1H, d, 10.1 Hz), 7.42-7.45 (2H, m), 7.76-7.85 (3H, m), 7.98-8.15 (2H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.19, 58.85, 67.62, 69.09, 70.50, 71.99, 76.15, 82.47, 126.13, 126.20, 127.68, 127.93, 128.42, 133.30, 134.53, 135.47, 135.67, 136.37, 136.72, 139.31, 139.72, 139.96, 139.99, 141.29, 141.48, 141.57, 141.65, 141.72, 141.85, 141.91, 142.07, 142.29, 142.33, 142.46, 142.78, 142.92, 144.14, 144.17, 144.36, 144.49, 144.91, 144.96, 145.07, 145.15, 145.30, 145.33, 145.52, 145.69, 145.87, 145.94, 145.98, 146.09, 146.23, 146.52, 147.04, 152.99, 153.28, 154.08, 156.19; IR (KBr, cm^{-1}) 2899, 2862, 2799, 1695, 1508, 1462, 1423, 1339, 1319, 1238, 1180, 1044, 858, 820, 745, 600, 575; MALDI-TOF-MS (matrix: SA) found

991.1564 (calcd for, $C_{77}H_{21}NO_2^+$, exact mass: 991.1572)

N-Methoxyethoxyethyl-2-(1-naphthyl)fulleropyrrolidine (1y):
^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.89-2.94 (1H, m), 3.43 (3H, s), 3.43-3.50 (1H, m), 3.62-3.65 (2H, m), 3.76-3.78 (2H, m), 3.96-4.00 (1H, m), 4.05-4.10 (1H, m), 4.49 (1H, d, J= 10.0 Hz), 5.31 (1H, d, J= 10.0 Hz), 6.16 (1H, s), 7.44-7.45 (2H, m), 7.62 (1H, t, J= 8.0 Hz), 7.83 (1H, d, J= 9.0 Hz), 7.87 (1H, d, J= 8.0 Hz), 8.39 (1H, d, J= 6.0 Hz), 8.52 (1H, d, J= 8.0 Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 51.98, 59.19, 67.71, 69.50, 70.51, 72.04, 76.29, 123.91, 125.52, 125.81, 126.11, 128.07, 128.63, 129.16, 132.65, 133.19, 133.99, 135.47, 135.87, 136.13, 136.66, 139.26, 139.49, 140.14, 140.34, 141.56, 141.64, 141.77, 141.97, 142.04, 142.11, 142.24, 142.27, 142.30, 142.56, 142.66, 142.93, 143.10, 144.23, 144.39, 144.57, 144.64, 145.09, 145.20, 145.25, 145.29, 145.44, 145.55, 145.68, 145.74, 145.92, 146.07, 146.20, 146.73, 147.04, 147.25, 147.31, 153.70, 154.17, 154.26, 156.81; IR (KBr, cm^{-1}) 2808, 1508, 1456, 1425, 1178, 1107, 773, 52; MALDI-TOF-MS (matrix: SA) found 991.203 (calcd for $C_{77}H_{21}NO_2$, exact mass: 991.173).

N-Methoxyethoxyethyl-2-(2-thiophene)fulleropyrrolidine (1z):
^{1}H NMR (400MHz,$CDCl_3$, J= Hz) δ 2.87-2.93 (1H, m), 3.39 (3H, s), 3.49-3.57 (1H, m), 3.60-3.62 (2H, m), 3.92-3.97 (1H, m), 4.00-4.05 (1H, m), 4.26 (1H, d, J= 9.8 Hz), 5.19 (1H, d, J= 9.8 Hz), 5.47 (1H, s), 6.99 (1H, t, J= 4.9 Hz), 7.31 (1H, d, J= 5.9 Hz), 7.34 (1H, d, J= 4.0 Hz); ^{13}C NMR (100MHz,$CDCl_3$)) δ 52.13, 58.78, 67.42, 68.86, 70.21, 70.53, 71.95, 75.56, 81.51, 125.34, 125.38, 129.53, 135.31, 135.75, 136.13, 136.79, 139.73, 139.98, 141.16, 141.30, 141.43, 141.53, 141.57, 141.69, 141.72, 141.76, 141.95, 141.98, 142.29, 142.33, 142.36, 142.45, 142.89, 144.05, 144.14, 144.29, 144.45, 144.89, 144.92, 144.92, 144.97, 145.04, 145.07, 145.09, 145.11, 145.18, 145.31, 145.33, 145.41, 145.66, 145.68, 145.83, 145.87, 145.92, 145.94, 146.00, 146.03, 146.04, 146.10, 147.00, 147.02, 152.14, 152.50, 153.58, 155.78; IR (KBr, cm^{-1}) 2864, 2812, 1462, 1427, 1180, 1107, 839, 768, 700, 527; MALDI-TOF-MS (matrix: SA) found 947.0978 (calcd for $C_{71}H_{17}NO_2S^+$, exact mass: 947.0980)