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Near-IR absorbing donor–acceptor charge-transfer gallium complex, an example from non-transition metal chemistry

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Contents

Experimental details

General information

3,5-Di-*tert*-butyl-*o*-benzoquinone, 2,2'-bipyridine, iodine were purchased from Sigma-Aldrich. 3,6-Di-*tert*-butyl-*o*-benzoquinone was synthesized according to the reported procedure [S1]. Solvents were purified following standard methods [S2]. All manipulations with solutions of complexes were performed under anaerobic conditions. IR spectra of the studied compounds were recorded on an FSM1201 Fourier-IR spectrometer in a nujol using KBr plates in the range 4000–400 cm^{-1}. NMR spectra were recorded in CD_3CN on a Bruker Avance Neo NMR spectrometer (300 MHz) with Me_4Si as the internal standard. UV/Vis spectra were measured on SHIMADZU UV-3600 spectrometers. Elemental analysis was performed with an Elementar Vario El cube instrument.

Synthesis

A mixture of 3,6-di-*tert*-butyl-*o*-benzoquinone (or 3,5-di-*tert*-butyl-*o*-benzoquinone) (0.15 g, 0.68 mmol) and iodine (0.086 g, 0.34 mmol) in THF (40 ml) was stirred intensively with gallium metal excess (3 g) at 50°C for 3 hours until the color of *o*-quinone disappeared completely. The resulting hot light-colored solution was decanted from excess metal and combined with a hot solution of bipy in toluene (0.11 g, 0.68 mmol) for 3,6-di-*tert*-butyl-*o*-benzoquinone or in THF (0.22 g, 1.36 mmol) for 3,5-di-*tert*-butyl-*o*-benzoquinone. The resulting complexes were isolated upon slow cooling of reaction mixtures as deep-red (**1**·PhMe) or orange (**2**·$(C_4H_8O)_4$) crystalline products.

Complex 1: the total yield of analytically pure product as crystals of **1**·PhMe is 0.37 g (82 %). Anal. calc. for $C_{31}H_{36}GaIN_2O_2$: C, 55.97; H, 5.45; N, 4.21 %. Found: C, 56.40; H, 5.81; N, 4.13 %. IR (Nujol, KBr) cm^{-1}: 1611(s), 1601(s), 1576, 1567, 1495, 1463(s), 1456(s), 1447(s), 1404(s), 1378(s), 1352, 1318(s), 1297, 1280(s), 1244(s), 1204, 1172, 1159(s), 1146, 1121, 1102, 1062(s), 1045, 1031(s), 977(s), 939(s), 924, 902, 829, 809, 792, 770(s), 732(s), 703(s), 652(s), 639, 612, 545, 484. ^{1}H NMR (20 °C, CD_3CN): δ 9.38 (d (J_{HH} = 4.8 Hz), 1H, H_{arom} of bipy), 8.91 (d (J_{HH} = 4.8 Hz), 1H, H_{arom} of bipy), 8.68-8.40 (m, 2H_{arom} of bipy), 8.32 (t (J_{HH} = 7.87 Hz), 1H,

H_{arom} of bipy), 7.99-7.85 (m, 2H, H_{arom} of bipy), 7.60 (t (J_{HH} = 6.5 Hz), 1H, H_{arom} of bipy), 7.28-7.15 (m, 5H, H_{arom} of toluene), 6.42 (s, 1H, H_{arom}), 6.28 (s, 1H, H_{arom}), 2.33 (s, 3H, Me-group of toluene), 1.45 (s, 9H, t-Bu), 1.16 (s, 9H, t-Bu).

Complex 2: the total yield of analytically pure product as crystals of **2**·$(C_4H_8O)_4$ is 0.59 g (86 %). Anal. calc. for $C_{50}H_{68}GaIN_4O_6$: C, 59.01; H, 6.73; N, 5.51 %. Found: C, 59.44; H, 6.77; N, 5.09 %. IR (Nujol, KBr) cm^{-1}: 1606 s, 1386 s, 1467 s, 1451 s, 1404 s, 1390 s, 1357 s, 1347 s, 1310 w, 1294 m, 1280 m, 1245 s, 1213(s), 1208(s), 1184(w), 1150 m, 1071 m, 1041 s, 1030 w, 1015 m, 973 s, 956 s, 937 m, 924 w, 831 m, 808 m, 785 m, 760 m, 701 s, 681 m, 652 m, 633 m, 612 w, 563 w, 498 w, 489 w. ^{1}H NMR (20 °C, CD_3CN): δ 9.00(d (J_{HH} = 5.6 Hz), 1H, H_{arom} of bipy), 8.91 (d (J_{HH} = 5.6 Hz), 1H, H_{arom} of bipy), 8.71-8.58 (m, 4H, H_{arom} of bipy), 8.50-8.43 (m, 2H, H_{arom} of bipy), 7.98 (t (J_{HH} = 6.2 Hz), 1H, H_{arom} of bipy), 7.90 (t (J_{HH} = 6.2 Hz), 1H, H_{arom} of bipy), 7.78 (d (J_{HH} = 5.6 Hz), 2H, H_{arom} of bipy), 7.74 (d (J_{HH} = 5.6 Hz), 2H, H_{arom} of bipy), 7.60 (t (J_{HH} = 6.2 Hz), 2H, H_{arom} of bipy), 6.51 (d (J_{HH} = 1.14 Hz), 1H, H_{arom}), 6.44 (d (J_{HH} = 1.14 Hz), 1H, H_{arom}), 3.64 (m, 16H, THF), 1.80 (m, 16H, THF), 1.19 (s, 18H, t-Bu).

Single-crystal X-ray diffraction analysis

The X-ray diffraction data were collected on a Bruker D8 Venture Photon single crystal diffractometer equipped with microfocus sealed tube Incoatec IμS 3.0 (Mo *Kα* radiation, λ = 0.71073 Å) in *φ*- and *ω*-scan mode at the Center of shared equipment IGIC RAS. The raw data for both experiments were treated with the APEX3 program suite [S3]; experimental intensities were corrected for absorption effects using SADABS program [S3]. The structures of **1**·PhMe and **2**·$(C_4H_8O)_4$ were solved by direct methods and refined by a full-matrix least-squares method using SHELX software package [S3]. All non-hydrogen atoms are refined anisotropically. In **2**·$(C_4H_8O)_4$, the C-C distances in the disordered THF molecule were restrained using DFIX and SADI commands, and the atomic displacement parameters (ADP) have been restrained using SIMU command. All of the H atoms were placed in calculated positions and refined in the "riding model" with U_{iso}(H) = 1.2U_{eq} of their parent atoms (U_{iso}(H) = 1.5U_{eq} for methyl groups). The X-ray quality crystals were obtained by slow cooling the solutions in a mixture THF/toluene

(1:1) or THF of **1**·PhMe and **2**·$(C_4H_8O)_4$, respectively. The unit cell of **1** contains one toluene molecule per molecule of the complex. The unit cell of **2** contains four THF molecules per molecule of the complex. The selected bond lengths and angles are presented in Table S1. The crystal data and some details of the data collection and refinement for **1**·PhMe and **2**·$(C_4H_8O)_4$ are listed in the article's main text. CCDC 2095157 (**1**·PhMe) and 2095158 (**2**·$(C_4H_8O)_4$) contain the supplementary crystallographic data for this paper. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44- 1223-336033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

DFT calculations

Density functional theory (DFT) calculations were performed using the Gaussian 09 program package[4] at the B3LYP/ Def2TZVP level. The stationary points on the potential energy surfaces were located by full geometry optimization with the calculation of the force constant matrix and checking for the stabilities of the DFT wave function.

Table S1. Selected bond lengths (Å) and angles (°) for the compounds **1**·PhMe and **2**·$(C_4H_8O)_4$.

Bond	**1**·PhMe	Bond	**2**·$(C_4H_8O)_4$
Ga(1)-O(1)	1.8687(17)	Ga(1)-O(1)	1.9040(16)
Ga(1)-O(2)	1.8832(17)	Ga(1)-O(2)	1.9154(16)
Ga(1)-N(1)	2.084(2)	Ga(1)-N(1)	2.080(2)
Ga(1)-N(2)	2.054(2)	Ga(1)-N(2)	2.0913(19)
I(1)-Ga(1)	2.5550(4)	Ga(1)-N(3)	2.0973(19)
		Ga(1)-N(4)	2.088(2)
O(1)-C(1)	1.362(3)	O(1)-C(1)	1.358(3)
O(2)-C(2)	1.354(3)	O(2)-C(2)	1.350(3)
C(1)-C(2)	1.417(4)	C(1)-C(2)	1.426(3)
C(2)-C(3)	1.409(3)	C(2)-C(3)	1.383(3)
C(3)-C(4)	1.399(4)	C(3)-C(4)	1.401(3)
C(4)-C(5)	1.381(4)	C(4)-C(5)	1.395(3)
C(5)-C(6)	1.393(4)	C(5)-C(6)	1.404(3)
C(1)-C(6)	1.398(4)	C(1)-C(6)	1.401(3)
C(6)-C(7)	1.540(4)	C(6)-C(7)	1.531(3)
C(3)-C(8)	1.528(4)	C(4)-C(8)	1.532(3)
		Angles	

O(1)-Ga(1)-O(2)	87.67(8)	O(1)-Ga(1)-O(2)	87.85(7)
O(1)-Ga(1)-N(2)	136.89(8)	O(1)-Ga(1)-N(1)	93.04(7)
O(2)-Ga(1)-N(2)	91.88(8)	O(2)-Ga(1)-N(1)	94.34(8)
O(1)-Ga(1)-N(1)	87.69(8)	O(1)-Ga(1)-N(4)	95.42(7)
O(2)-Ga(1)-N(1)	158.78(8)	O(2)-Ga(1)-N(4)	93.05(7)
N(1)-Ga(1)-N(2)	77.59(9)	N(1)-Ga(1)-N(4)	168.97(8)
O(1)-Ga(1)-I(1)	116.27(6)	O(1)-Ga(1)-N(2)	91.46(7)
O(2)-Ga(1)-I(1)	103.89(6)	O(2)-Ga(1)-N(2)	172.11(7)
N(2)-Ga(1)-I(1)	105.65(6)	N(1)-Ga(1)-N(2)	77.85(8)
N(1)-Ga(1)-I(1)	96.73(6)	N(4)-Ga(1)-N(2)	94.84(7)
		O(1)-Ga(1)-N(3)	172.85(8)
		O(2)-Ga(1)-N(3)	90.84(7)
		N(1)-Ga(1)-N(3)	94.06(8)
		N(4)-Ga(1)-N(3)	77.63(8)
		N(2)-Ga(1)-N(3)	90.79(7)

Table S2. Calculated total energy and atomic coordinates for complex **1**.

E_{total} = -3414.6809188 a.u.

Atomic number	X	Y	Z
53	1.564571	-0.000702	2.617226
31	0.567783	0.000173	0.231981
8	-0.746693	1.300615	-0.110735
8	-0.746274	-1.300394	-0.111192
7	1.991021	-1.303196	-0.728436
7	1.990693	1.303954	-0.727361
6	-1.961684	0.709208	-0.241227
6	-3.150461	1.443260	-0.376010
6	-4.320441	0.694015	-0.514892
1	-5.270139	1.196791	-0.623827
6	-4.320225	-0.694889	-0.515030
1	-5.269781	-1.197936	-0.624023
6	-3.150009	-1.443794	-0.376290
6	-1.961466	-0.709369	-0.241427
6	-3.157093	2.980509	-0.371076
6	-4.575761	3.555637	-0.512567
1	-5.046240	3.256263	-1.450993
1	-4.525976	4.646901	-0.500688
1	-5.224046	3.245505	0.308958
6	-2.323396	3.513260	-1.556138
1	-1.301222	3.142081	-1.516287
1	-2.299648	4.607056	-1.543477
1	-2.761599	3.197229	-2.505658
6	-2.575284	3.508425	0.957925
1	-3.190155	3.184181	1.800305
1	-2.558745	4.602370	0.955546
1	-1.563603	3.143582	1.121908
6	-3.156111	-2.981046	-0.371677
6	-2.574085	-3.509055	0.957205
1	-1.562485	-3.143994	1.121200
1	-2.557267	-4.602993	0.954625

1	-3.188995	-3.185114	1.799669
6	-2.322316	-3.513305	-1.556874
1	-2.760673	-3.197259	-2.506323
1	-2.298210	-4.607098	-1.544412
1	-1.300262	-3.141800	-1.517027
6	-4.574594	-3.556638	-0.513180
1	-5.222884	-3.247007	0.308527
1	-4.524415	-4.647884	-0.501671
1	-5.045288	-3.257111	-1.451451
6	1.860558	-2.629812	-0.692337
1	0.956179	-2.999361	-0.229326
6	2.823653	-3.470838	-1.227805
1	2.689393	-4.542186	-1.182204
6	3.946591	-2.903943	-1.815691
1	4.719248	-3.530223	-2.242268
6	4.070832	-1.523390	-1.857403
1	4.935621	-1.069295	-2.317751
6	3.064757	-0.739023	-1.300128
6	3.064404	0.740505	-1.299821
6	4.069783	1.525566	-1.857374
1	4.934443	1.072050	-2.318533
6	3.944932	2.906038	-1.815059
1	4.717049	3.532844	-2.241844
6	2.822045	3.472189	-1.226351
1	2.687310	4.543457	-1.180285
6	1.859599	2.630539	-0.690746
1	0.955217	2.999453	-0.227270

Table S3. Calculated total energy and atomic coordinates for cation of **2**.

E_{total} = -3612.2344964 a.u.

Atomic number	X	Y	Z
31	-0.941919	0.112542	-0.115937
8	0.390179	-0.737572	0.914773
8	0.398832	0.968464	-1.121420
7	-1.166946	-1.508466	-1.494666
7	-2.474811	-1.145111	0.769725
7	-2.475698	1.347720	-1.036322
7	-1.211997	1.738055	1.250864
6	1.611118	-0.352062	0.442073
6	2.828827	-0.820790	0.956728
6	4.004981	-0.312547	0.383809
1	4.946387	-0.659410	0.774076
6	4.022013	0.612956	-0.659652
6	2.793517	1.048783	-1.162162
1	2.733379	1.762125	-1.974380
6	1.605363	0.574437	-0.630800
6	2.872269	-1.862291	2.091370
6	2.175354	-3.160556	1.629758
1	1.139708	-2.972195	1.352207
1	2.190216	-3.904318	2.430959
1	2.693726	-3.586803	0.768010
6	2.162483	-1.317232	3.349194
1	2.217603	-2.046953	4.161116
1	1.112249	-1.112360	3.148332
1	2.643151	-0.398657	3.694526
6	4.308481	-2.228156	2.498762
1	4.872040	-2.658524	1.669474
1	4.277432	-2.973102	3.296317
1	4.860087	-1.365199	2.875849
6	5.325365	1.157618	-1.267431
6	6.578292	0.569075	-0.602185
1	7.471604	0.991074	-1.066503
1	6.629281	-0.515280	-0.717602
1	6.620677	0.802053	0.463313
6	5.372379	2.691006	-1.097986
1	5.347772	2.966142	-0.041440
1	4.528958	3.178201	-1.589215
1	6.290134	3.095619	-1.531744
6	5.379632	0.814087	-2.770645
1	4.539195	1.246955	-3.315051
1	5.356628	-0.267143	-2.922151
1	6.299533	1.198934	-3.217505
6	-0.381175	-1.613628	-2.569936
1	0.201049	-0.732948	-2.808781
6	-3.094841	1.059981	-2.182617

1	-2.858891	0.103667	-2.627972
6	-0.313049	-2.784970	-3.309872
1	0.333434	-2.839866	-4.174200
6	-3.988596	1.928929	-2.786622
1	-4.464621	1.655791	-3.717609
6	-1.073780	-3.871503	-2.903664
1	-1.036693	-4.804467	-3.450395
6	-4.244951	3.144375	-2.168249
1	-4.937605	3.851073	-2.605784
6	-1.875380	-3.759984	-1.774517
1	-2.453502	-4.607375	-1.438169
6	-3.598564	3.446896	-0.979856
1	-3.789255	4.388315	-0.487383
6	-1.900188	-2.555222	-1.081170
6	-2.707276	2.527871	-0.432534
6	-2.680837	-2.325694	0.156881
6	-1.951636	2.772666	0.817851
6	-3.569237	-3.258289	0.685292
1	-3.738837	-4.200036	0.185739
6	-1.955813	3.981711	1.504237
1	-2.539599	4.818669	1.152071
6	-4.239467	-2.969262	1.863920
1	-4.929961	-3.686853	2.286881
6	-1.176659	4.111854	2.646847
1	-1.162815	5.048509	3.188323
6	-4.009502	-1.753281	2.491569
1	-4.504709	-1.490422	3.415483
6	-0.408213	3.038640	3.072856
1	0.222153	3.106976	3.948036
6	-3.117142	-0.870123	1.906473
1	-2.901371	0.087337	2.359769
6	-0.447116	1.862241	2.338898
1	0.145091	0.993901	2.595694

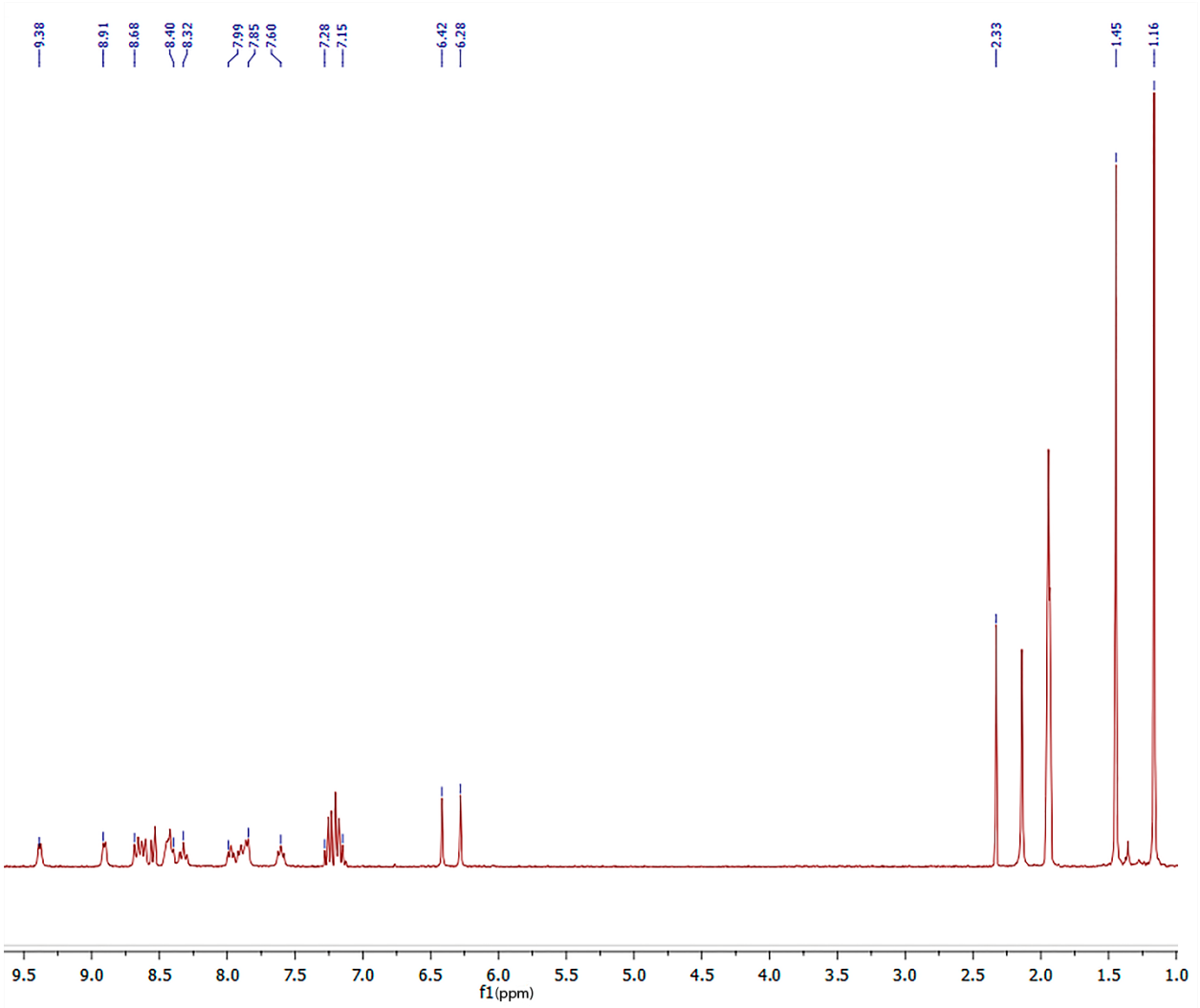

Figure S1. ^{1}H NMR spectrum of complex **1·PhMe** in CD_3CN.

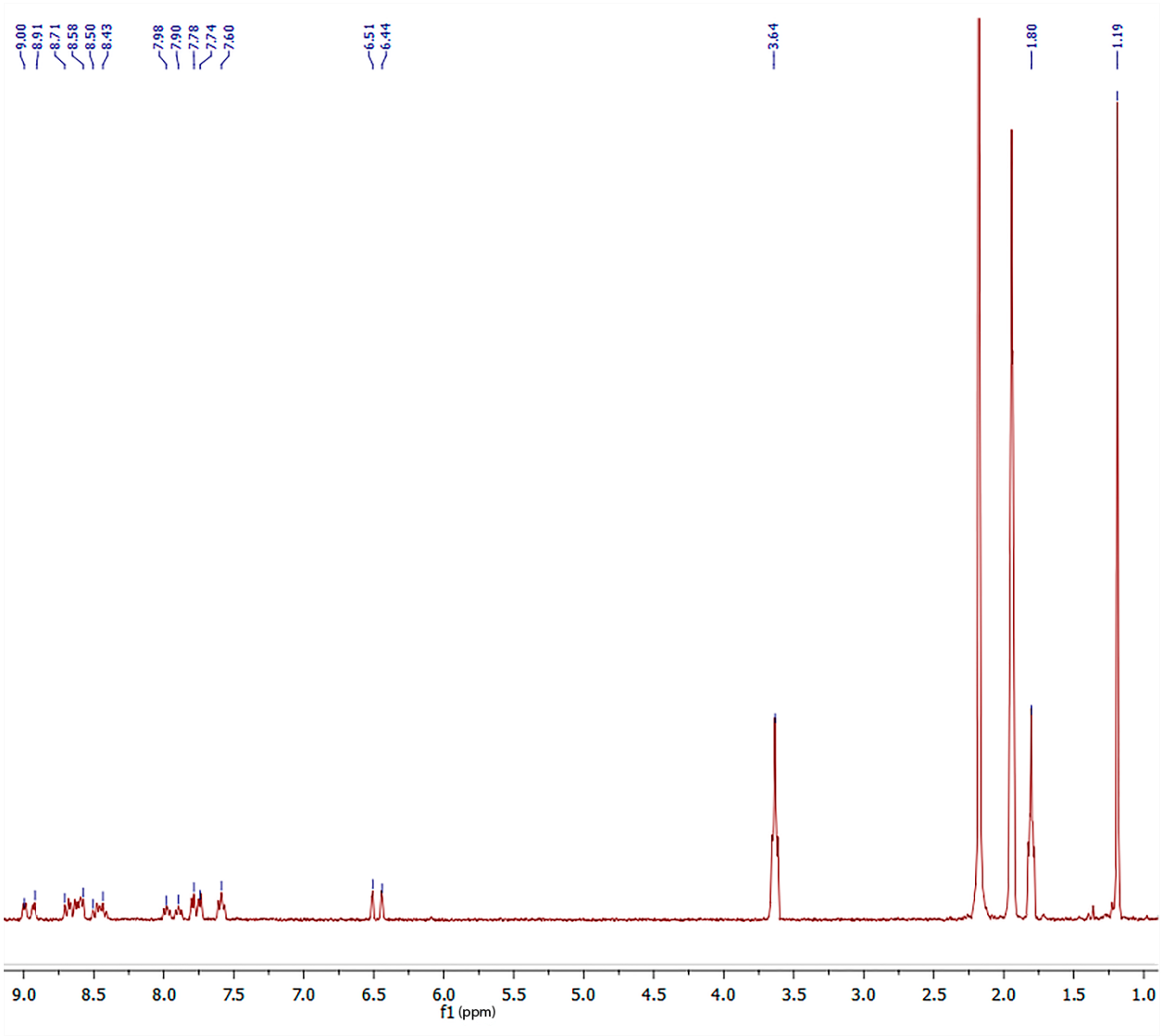

Figure S2. ^{1}H NMR spectrum of complex **2**·$(C_4H_8O)_4$ in CD_3CN.

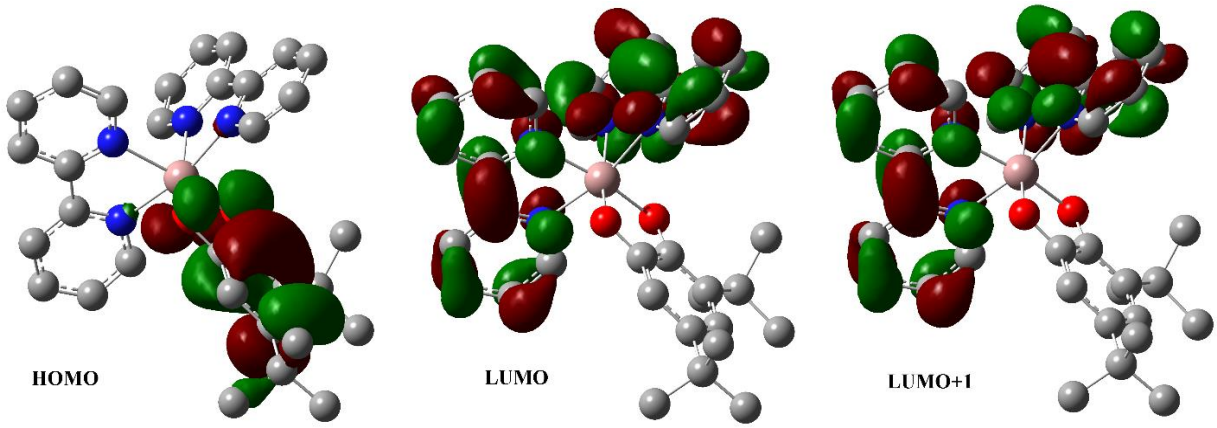

Figure S3. Frontier orbitals for the cation of complex **2** according to DFT calculations at the B3LYP/Def2TZVP level of theory. Isovalue = 0.03 a.u. The H atoms are omitted for clarity.

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