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Supporting Information

Complexes of guest-host type between C_{60} and group 9 metalloporphyrins

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1. Experimental

General Procedures and Instrumentation

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Ir^{III}(ttp)Ph[1] and Co^{III}(ttp)Ph[2] were prepared according to the literature procedures.

^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded on a a Bruker AV-400 instrument at 400 and 100 MHz, respectively. Chemical shifts were referenced with the residual solvent protons in C_6D_6 (δ 7.15 ppm) in ^{1}H NMR spectra as the internal standards and in $CDCl_3$ (δ 77.16 ppm) in $^{13}C\{^{1}H\}$ NMR spectra as the internal standards. Chemical shifts (*δ*) are reported in hertz (Hz). Coupling constants (*J*) were reported in Hertz (Hz).

All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 296 K on a Bruker SMART 1000 CCD diffractometer using MoK_α radiation. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F2 using the SHELXTL program package. All hydrogen atoms were geometrically fixed using the riding model.

Preparation of 1:1 stoichiometric ratio of C_{60} and Ir^{III}(ttp)Ph. Ir^{III}(ttp)Ph (2.5 mg, 0.00266 mmol) was dissolved in toluene (1.5 mL) to give a red solution. C_{60} (2.0 mg, 0.00278 mmol) was added into the solution. The solution mixture was treated in an ultrasonic cleaner (47kHz) for 1 min to give a dark brown solution. The single crystal obtained, namely $C_{60}\cdot 3Ir^{III}$(ttp)Ph, for X-ray diffraction analysis was grown from slow diffusion of hexane vapour into the above toluene solution in the dark using vial in a vial method. Samples for ^{1}H and ^{13}C{^{1}H} NMR analysis were prepared separately in benzene-d_6 and $CDCl_3$, respectively. ^{1}H NMR (400 MHz, C_6D_6): δ 1.08 (d, 2 H, *J* = 8.0 Hz), 2.40 (s, 12 H), 4.92 (t, 2 H, *J* = 7.6 Hz), 5.24 (t, 1 H, *J* = 7.2 Hz), 7.20 (d, 4 H, *J* = 8.0 Hz), 7.27 (d, 4 H, *J* = 7.6 Hz), 7.88 (dd, 4 H, *J* = 7.6 Hz, 1.6 Hz), 7.97 (d, 4 H, *J* = 7.2 Hz), 8.77 (s, 8 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.7, 120.2, 123.2, 123.9, 127.5, 127.6, 128.8, 131.7, 133.6, 134.1, 137.3, 137.6 (coordinated C_{60}), 138.8, 142.8.

Preparation of 2:1 stoichiometric ratio of C_{60} and Ir^{III}(ttp)Ph. Ir(ttp)Ph (2.5 mg, 0.00266 mmol) was dissolved in toluene (1.5 mL) to give a red solution. C_{60} (4.0 mg, 0.00532 mmol) was added into the solution. The solution mixture was treated in an ultrasonic cleaner (47kHz) for 1 min to give a dark brown solution. The single crystal obtained, namely C_{60}·Ir^{III}(ttp)Ph, for X-ray diffraction analysis was grown from slow diffusion of hexane vapour into the above toluene solution in the dark using vial in a vial method. Due to the poor quality of single crystal, the X-ray analysis data obtained from below was presented.

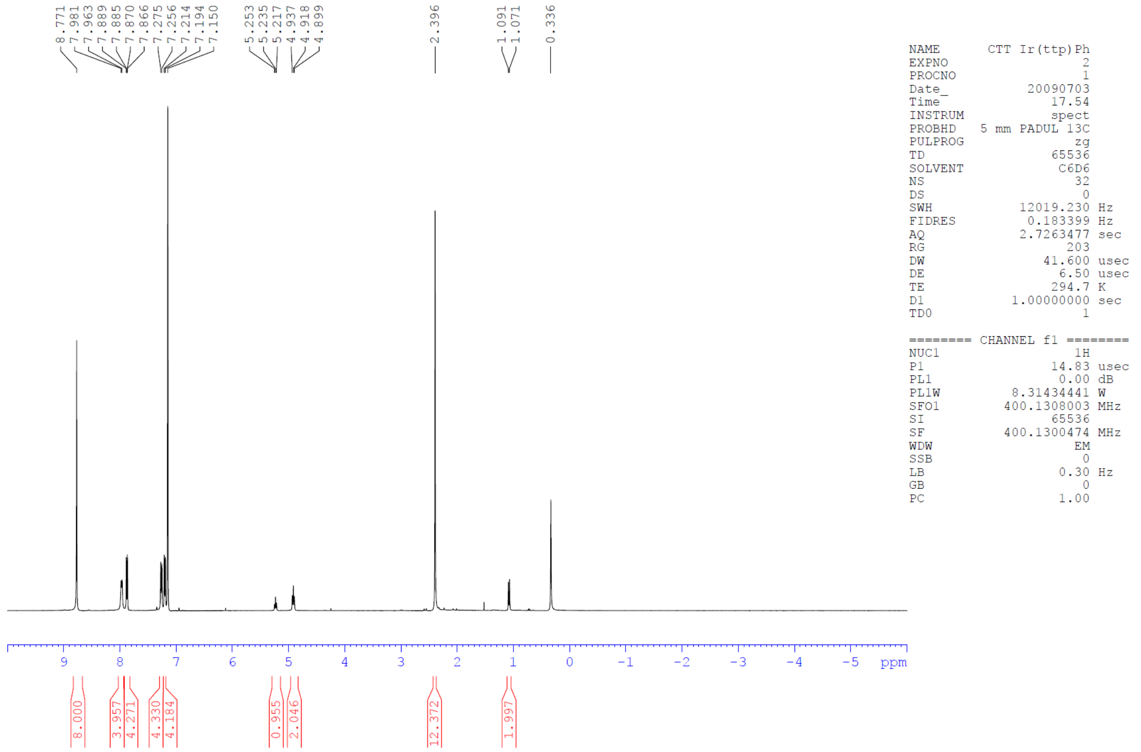
Preparation of 3:1 stoichiometric ratio of C_{60} and Ir^{III}(ttp)Ph. Ir(ttp)Ph (2.5 mg, 0.00266 mmol) was dissolved in toluene (1.5 mL) to give a red solution. C_{60} (6.0 mg, 0.00833 mmol) was added into the solution. The solution mixture was treated in an ultrasonic cleaner (47kHz) for 1 min to give a dark brown solution. The single crystal obtained, namely C_{60}·Ir^{III}(ttp)Ph, for X-ray diffraction analysis was grown from slow diffusion of hexane vapour into the above toluene solution in the dark using vial in a vial method. Samples for ^{1}H and ^{13}C{^{1}H} NMR analysis were prepared separately in benzene-d_6 and $CDCl_3$, respectively. ^{1}H NMR (400 MHz, C_6D_6): δ 1.10 (d, 2 H, *J* = 8.4 Hz), 2.39 (s, 12 H), 4.93 (t, 2 H, *J* = 7.4 Hz), 5.24 (t, 1 H, *J* = 7.2 Hz), 7.20 (d, 4 H, *J* = 7.6 Hz), 7.27 (d, 4 H, *J* = 7.2 Hz), 7.88 (d, 4 H, *J* = 7.6 Hz), 7.99 (d, 4 H, *J* = 6.8 Hz), 8.78 (s, 8

H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 21.7, 120.5, 123.2, 123.8, 127.5, 127.7, 128.1, 132.0, 133.5, 133.9, 137.3, 138.9, 139.6 (coordinated C_{60}), 142.4.

Preparation of 1:1 stoichiometric ratio of C_{60} and Co^{III}(ttp)Ph. Co^{III}(ttp)Ph (2.2 mg, 0.00273 mmol) was dissolved in toluene (1.5 mL) to give a red solution. C_{60} (2.0 mg, 0.00278 mmol) was added into the solution. The solution mixture was treated in an ultrasonic cleaner (47kHz) for 1 min to give a dark brown solution. The single crystal obtained, namely toluene·C_{60}·Co^{III}(ttp)Ph, for X-ray diffraction analysis was grown from slow diffusion of hexane vapour into the above toluene solution in the dark using vial in a vial method.

2. NMR Spectra

^{1}H NMR Spectrum of C_{60}:Ir^{III}(ttp)Ph = 1:1 (C_6D_6, 400 MHz)



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PROCNO                 1
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PULPROG               zg
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     0
SWH            12019.230 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   203
DW                41.600 usec
DE                  6.50 usec
TE                 294.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.83 usec
PL1                 0.00 dB
PL1W          8.31434441 W
SFO1         400.1308003 MHz
SI                 65536
SF           400.1300474 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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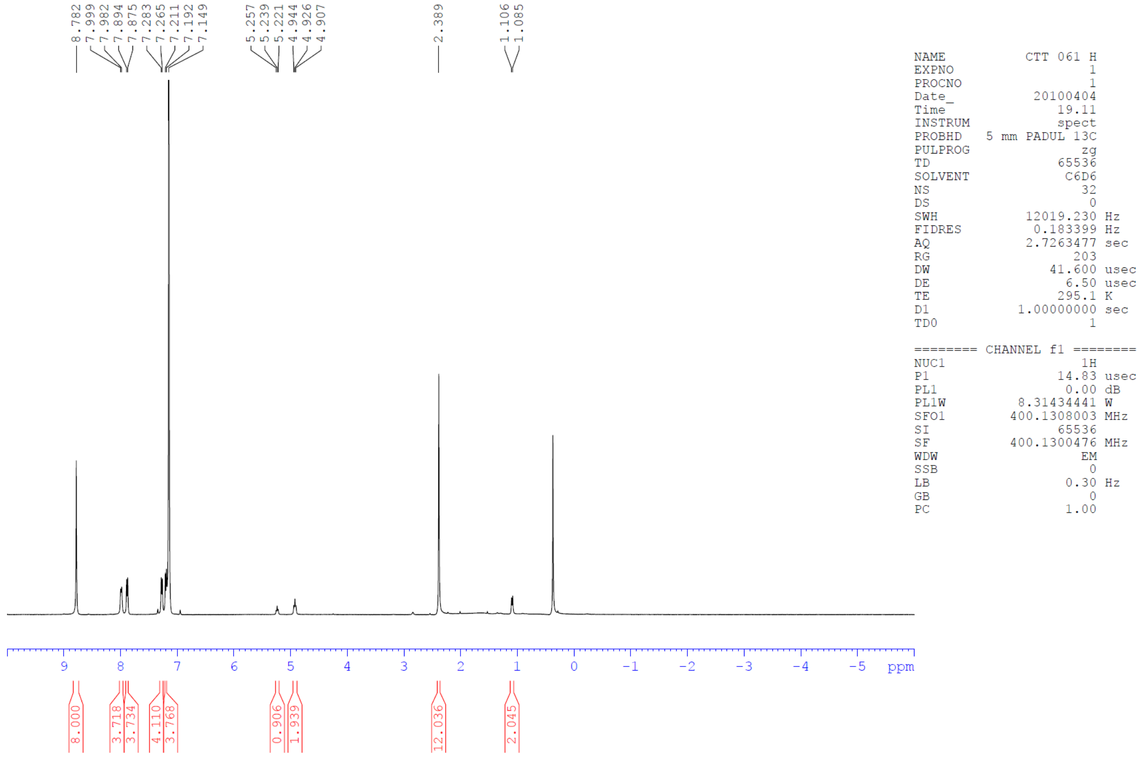
^{1}H NMR Spectrum of C_{60}:Ir^{III}(ttp)Ph = 3:1 (C_6D_6, 400 MHz)



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PULPROG               zg
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     0
SWH            12019.230 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   203
DW                41.600 usec
DE                  6.50 usec
TE                 295.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.83 usec
PL1                 0.00 dB
PL1W          8.31434441 W
SFO1         400.1308003 MHz
SI                 65536
SF           400.1300476 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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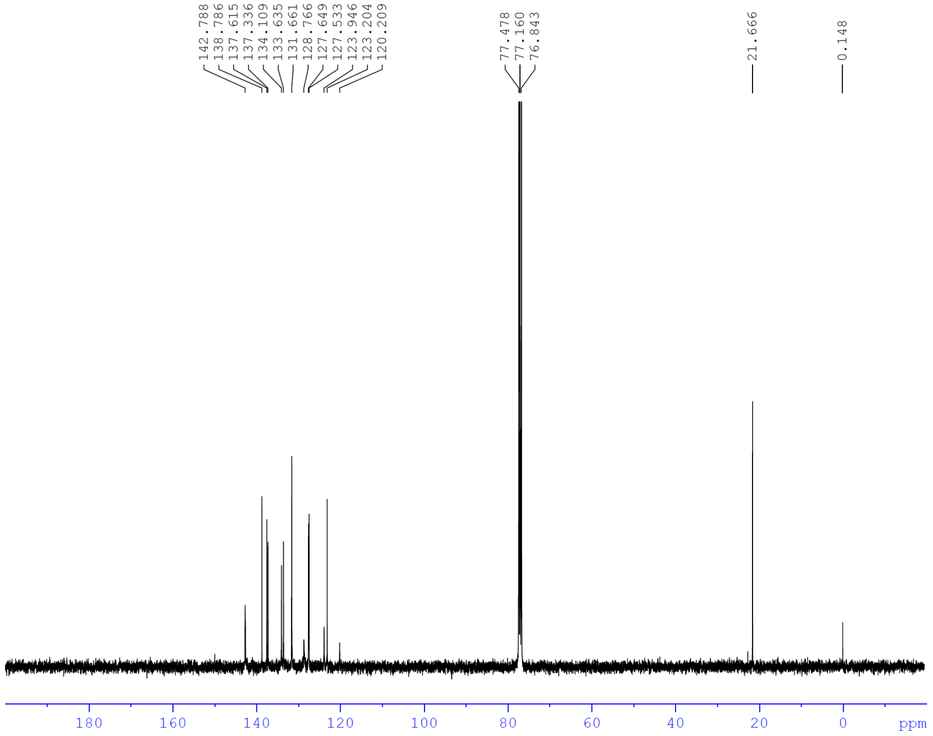
$^{13}C\{^1H\}$ NMR Spectrum of C_{60}:Ir^{III}(ttp)Ph = 1:1 ($CDCl_3$, 100 MHz)



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PROCNO                1
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PULPROG         zgpg30
TD               65536
SOLVENT           C6D6
NS                2622
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 203
DW              20.800 usec
DE                6.50 usec
TE               295.3 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.68 usec
PL1              -0.60 dB
PL1W       41.24164963 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               0.00 dB
PL12             15.66 dB
PL13             15.92 dB
PL2W        8.31434441 W
PL12W       0.22585411 W
PL13W       0.21272963 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127599 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
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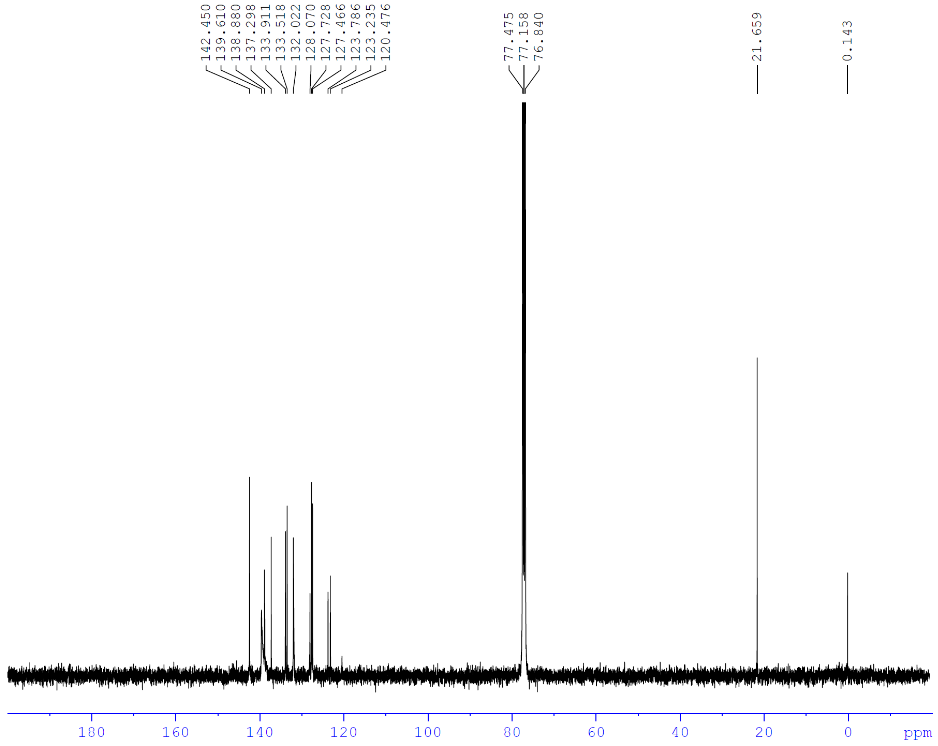
$^{13}C\{^1H\}$ NMR Spectrum of C_{60}:Ir^{III}(ttp)Ph = 3:1 ($CDCl_3$, 100 MHz)



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PROCNO                1
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PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS               12210
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 203
DW              20.800 usec
DE                6.50 usec
TE               295.5 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.68 usec
PL1              -0.60 dB
PL1W       41.24164963 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               0.00 dB
PL12             15.66 dB
PL13             15.92 dB
PL2W        8.31434441 W
PL12W       0.22585411 W
PL13W       0.21272963 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127545 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

3. X-Ray Crystallographic Data

Table S1. Crystal data and summary of data collection and refinement

	$C_{60}\cdot Ir^{III}$(ttp)Ph	$C_{60}\cdot 3Ir^{III}$(ttp)Ph	$C_{60}\cdot Co^{III}$(ttp)Ph/C_7H_8
CCDC nounber	1573104	1573102	1573103
color, shape	red, block	red, block	red, block
empirical formula	$C_{114}H_{41}N_4Ir$	$C_{222}H_{123}N_{12}Ir_3$	$C_{121}H_{49}N_4Co$
formula wt	1658.71	3534.92	1617.64
temp (K)	296(2)	296(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	C2/c	P-1	C2/c
unit cell dimens			
a (Å)	16.3792(7)	18.078(3)	16.367(3)
b (Å)	22.5894(10)	19.791(4)	22.892(4)
c (Å)	21.6432(10)	27.758(5)	21.508(4)
α (deg)	90	89.910(4)	90
β (deg)	94.0580(10)	89.021(3)	93.794(4)
γ (deg)	90	64.574(3)	90
volume (Å^3)	7987.8(6)	8968(3)	8041(3)
Z	4	2	4
calcd density (g cm^{-3})	1.379	1.309	1.297
abs coeff (mm^{-1})	1.728	2.278	0.272
F(000)	3320	3540	3224
cryst size (mm)	0.400 x 0.300 x 0.200	0.400 x 0.300 x 0.200	0.400 x 0.300 x 0.200
θ range for data collection (deg)	1.538 to 25.247	0.734 to 25.000	1.758 to 25.250
limiting indices	-19<=h<=19 -27<=k<=27 -25<=l<=25	-20<=h<=18 -23<=k<=23 -33<=l<=33	-19<=h<=19 -27<=k<=27 -25<=l<=25
no. of rflns collected	50527	103733	44095
independent rflns	7240 [R(int) = 0.0464]	30498 [R(int) = 0.0653]	7279 [R(int) = 0.0869]
completeness to θ = 25.242	99.8%	94%	99.8%
absorp corr	semi-empirical from equivalents	multi-scan	multi-scan
max. and min. transmn	0.7456 and 0.6166	0.7456 and 0.6360	0.7456 and 0.6579
refinement method	full-matrix least-squares on F^2		
no. of data/ restraints / params	7240/15/538	30498/20/2134	7079/47/601
GOF	1.115	1.123	1.235
final R indices [I>2σ(I)]	R_1 = 0.0335 wR_2 = 0.0859	R_1 = 0.1019 wR_2 = 0.3007	R_1 = 0.1127 wR_2 = 0.3073
R indices (all data)	R_1 = 0.0377 wR_2 = 0.0874	R_1 = 0.1318 wR_2 = 0.3200	R_1 = 0.1419 wR_2 = 0.3307
largest diff. peak and hole (e Å^{-3})	1.398 and -1.902	7.967 and -4.310	3.156 and -0.464

4. References

1. C. W. Cheung and K. S. Chan, *Organometallics*, 2011, **30**, 4269-4283.

2. C. R. Liu, Y. Y. Qian and K. S. Chan, *Dalton Trans.*, 2014, **43**, 7771-7779.