Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2011

To cite this article: Se Won Park, Ho Wan Ham & Young Sik Kim (2011): Theoretical Studies of Mono-Cyclometalated Ir(III) Complexes with Phenylpyrazole Based Ligands and Phosphines, Molecular Crystals and Liquid Crystals, 551:1, 24-32

To link to this article: http://dx.doi.org/10.1080/15421406.2011.600123

Mol. Cryst. Liq. Cryst., Vol. 551: pp. 24–32, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.600123

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Theoretical Studies of Mono-Cyclometalated Ir(III) Complexes with Phenylpyrazole Based Ligands and Phosphines

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New blue emitting mixed ligand iridium(III) complexes comprising one cyclometalating, two phosphines trans to each other such as Ir(dppzc)(PPhMe$_2$)$_2$(H)(L) (L = Cl, CN) [dppzc = 1,3-Diphenyl-1H-pyrazole-4-carboxaldehyde] were studied to tune the phosphorescence wavelength to the deep blue region and to enhance the luminescence efficiencies. We investigate the electron-withdrawing capabilities of ancillary ligands using the DFT and TD-DFT calculations on the ground and excited states of the complexes. From these results, we discussed how the ancillary ligand influences the emission peak as well as the metal to ligand charge transfer (MLCT) transition efficiency. The calculated energies of triplets are 3.09 and 3.16 eV, respectively, which are all higher than that of Ir(dfppy)$_2$(acac) and FIrpic known as blue phosphorescence materials with 2.69 and 2.73 eV.

Keywords Blue Phosphorescence; OLEDs; one cyclometalating Ir(III); mixed ancillary ligands; TDDFT.

Introduction

Organic light-emitting diodes (OLEDs) have attracted increasing attention in recent years and hold promise as the next generation of flat-panel displays due to the OLEDs' low-voltage operation, wide-viewing angle, high contrast, and mechanical flexibility. Organic material emits visible light in a multilayered structure when a bias voltage is applied to the structure, OLEDs and emitting materials have developed rapidly. Luminescent materials for OLED devices are generally classified in two groups: fluorescent and phosphorescent. OLEDs based on phosphorescent materials can greatly improve electroluminescence performance because both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100%.[1–3] Heavy metals, such as Ir or Pt, present in the complexes are known to induce an intersystem crossing by strong spin-orbit coupling. This crossing leads to a mixing of the singlet and triplet excited states.[4–7] Radiative relaxation of the spin-forbidden nature from the triplet excited state is then allowed, resulting in high phosphorescence efficiencies. Thus, heavy metal complexes can serve as efficient phosphors in OLEDs. Unfortunately, most phosphorescent emitters have a long radiative lifetime, which leads to the dominant triplet-triplet (T-T) annihilation at high currents. The occurrence of T-T annihilation diminishes

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the performance of phosphorescent material, particularly its maximum brightness and luminescence efficiency at high currents.[8,9]

Recently, many theoretical approaches using density functional theory (DFT) such as B3LYP and B3PW91 have processed to describe the ground state properties of organometallic and inorganic molecules.[10,11] Also, applications of time-dependent DFT method (TD-DFT)[12,13] which calculated the excited states of molecules have recently begun to estimate vertical excitation on transition metal complexes.[14,15]

In this study, to gain insight into the factors responsible for the emission color change and the different luminescence efficiency; we investigate the electron-withdrawing capabilities of ancillary ligands using the DFT and TD-DFT calculations on the ground and excited states of the complexes. From these results, we discuss how the ancillary ligand influences the emission peak as well as the MLCT transition efficiency.

Computational Methods

Molecular orbital calculations. The ground and low-lying excited electronic states of iridium (III) complexes were calculated using the Gaussian 98 and 03 program package. For the calculated ground state geometries, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). Hartree-Fock (HF) method with 3–21G(d) basis set and Becke-Lee-Young-Parr composite exchange correlation functional (B3LYP) method with the 6–31G(d) basis set were used for the geometry optimization and the energy level calculation of the ground state of those ligands, respectively. Calculations on the electronic ground states of the iridium (III) complexes have been carried out using the same calculation method except LANL2DZ basis set for an iridium atom.

Electron population measurements. The electronic populations on the central atom were calculated to show the significant admixture of ligand π character with the amount of iridium 5d character in the occupied molecular orbitals related to those MLCT transitions.

Absorption spectra measurements. To obtain the vertical excitation energies of the low-lying singlet and triplet excited states of the complexes, TDDFT calculations using the B3LYP functional was performed at the respective ground-state geometry, where the basis set of ligands was changed to 6–31+G(d). Typically, the lowest 10 triplet and 10 singlet roots of the nonhermitian eigenvalue equations were obtained to get the vertical excitation energies and compared with the absorption spectra to examine each peak. The ground-state B3LYP and excited-state TDDFT calculations were carried out using Gaussian 98 and Gaussian 03 programs.

Results and Discussion

The colors of the phosphorescent complexes used in OLEDs are tuned by varying both cyclometalating and ancillary ligands. Several small molecular and polymeric blue-emitting phosphorescent complexes have been reported, but the realization of highly efficient deep blue emission remains a challenge. For the common phenylpyrazole (ppz) cyclometalating ligand, the highest occupied molecular orbital (HOMO) is localized on the phenyl π and iridium 5d orbitals, while the lowest unoccupied molecular orbital (LUMO) is localized on the π^* orbitals of the pyrazole ring. To achieve deep blue emission and to improve the

emission efficiency, it is necessary to remodel the ppz ligand as: (1) substitution of phenyl group and carboxaldehyde group of the pyrazole ring that lower the triplet energy enough that the quenching channel is not thermally accessible, and (2) changing ancillary ligands coordinated to iridium atom to phosphine and cyano groups known as very strong field ligands. Their inclusion in the coordination sphere causes a large d-orbital energy splitting to improve the luminescence efficiency and increase the HOMO-LUMO gap to achieve the hypsochromic shift in emission color.

After optimizations of molecular structures using density functional theory (DFT), energy levels and d-orbital characteristics of HOMOs and LUMOs of iridium complexes were investigated. The structures for iridium (III) complexes in this study are shown in Figure 1. Calculated HOMO, LUMO level and energy gap of iridium (III) complexes are shown in Figure 2. Phenyl group and carboxaldehyde group substituted on the pyrazole ring lower LUMO energy level enough that the quenching channel is not thermally accessible. Ancillary ligands coordinated to iridium atom to phosphine and cyano groups can lower HOMO energy level, which causes a large d-orbital energy splitting to improve the luminescence efficiency and also increase the HOMO-LUMO gap to achieve the hypsochromic shift in emission color.

Interestingly, ancillary ligands alter the MLCT energy, mainly by changing the HOMO energy level. The strong field ancillary ligand, such as CN^-, $PPhMe_2$ lower the HOMO energy level more than the weak field ancillary ligand, Cl^-. The HOMO energy level may then be lowered by strong-field ancillary ligands, which causes large d-orbital energy splitting.

To examine which ligand mainly contributes to the MLCT transition process of these complexes, the d-orbital characteristics of HOMOs and LUMOs were investigated after

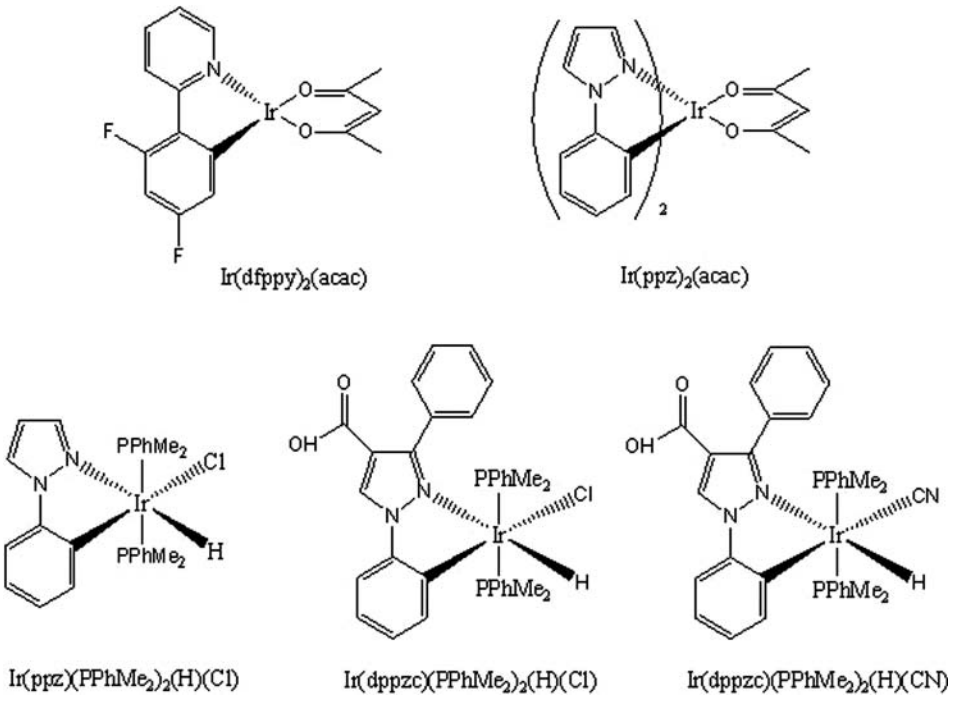

Figure 1. The structure of the mono-cyclometalated iridium (III) complexes.

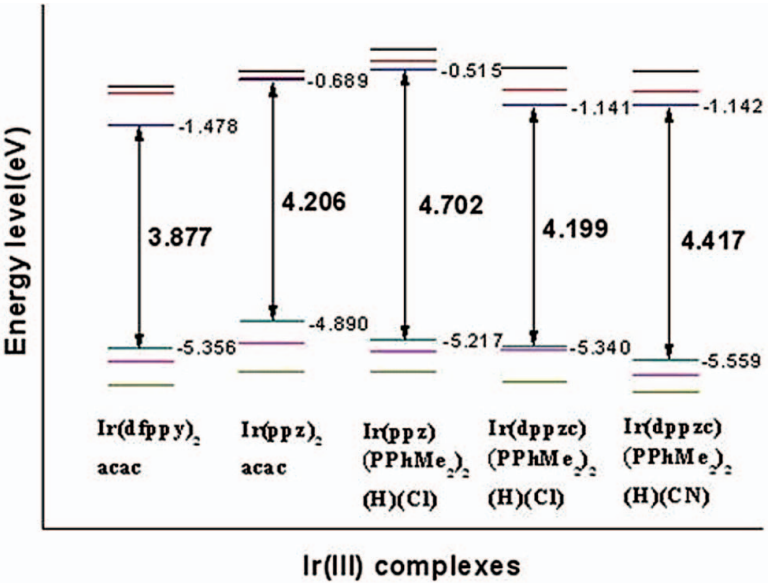

Figure 2. Schematic drawing of orbital energies of highest occupied and lowest unoccupied MOs of iridium (III) complexes.

geometry optimization of the molecular structure of these complexes using DFT. Molecular structure (length of Ir-C, Ir-N and Ir-ancillary ligands) and electronic populations of 5d orbital of iridium ion in HOMOs and LUMOs are shown in Table 1. The electronic populations of iridium atom orbitals in three highest MOs are 31% $\sim$ 68% in the case of Ir(dppzc)$(PPhMe_2)_2$(H)(CN). These are more than those of Ir$(ppz)_2$(acac), which are 37% $\sim$ 50% and similar to those of Ir$(ppy)_2$(acac), which are 45% $\sim$ 67%.[16,17] This shows that the strong field ancillary ligand such as CN^-, $PPhMe_2$ increases the MLCT characteristics by lowering the t_{2g} energy level of the 5d-orbitals of the metal to increase the mixing between the metal and the dppzc ligand. It is also likely that strong-field ancillary ligands lengthen the bond lengths of Ir–C(ppz) trans to the ancillary ligand, which lowers the energy levels of the dπ-orbitals of the metal. Comparison of the calculated bond lengths for Ir(dppzc)$(PPhMe_2)_2$(H)(Cl) and Ir(dppzc)$(PPhMe_2)_2$(H)(CN) are 2.040 Å and 2.101 Å, respectively.

Contour plots of the three highest HOMOs and the three lowest LUMOs of Ir(dppzc)$(PPhMe_2)_2$(H)(Cl) and Ir(dppzc)$(PPhMe_2)_2$(H)(CN) are shown in Figure 3. For iridium complexes, the LUMO and LUMO+1 originated from dppzc π^* orbitals, which is consistent with the invariance of their energy levels. Further, the LUMO+2 are localized at the π^* orbitals of $PPhMe_2$. The HOMO of iridium complexes are formed from a combination of iridium 5d and dppzc π orbitals, while the HOMO-1 are formed from a combination of iridium 5d and Cl 2p (or CN π) orbitals. These orbitals are important because dominant excitations and emissions mainly occur by the electronic transition among these orbitals.

TD-DFT calculations were employed to examine the low-lying singlet and triplet states of Ir$(dfppy)_2$(acac), FIrpic, Ir(dppzc)$(PPhMe_2)_2$(H)(Cl) and Ir(dppzc)$(PPhMe_2)_2$(H)(CN). The calculated excitation energies, dominant orbital excitation obtained and oscillator strengths are shown in Table 2. Phenyl group and carboxaldehyde group substituted on the pyrazole ring lower LUMO energy level enough that the quenching channel is not accessible.

Table 1. Molecular structure (length of Ir-C, Ir-N and Ir-ancillary ligands) and electronic populations of 5d orbital of iridium ion in HOMOs & LUMOs of Ir(dppzc)($PPhMe_2$)$_2$(H)(Cl) and Ir(dppzc)($PPhMe_2$)$_2$(H)(CN).

Complexes	Ir-C Ir-N Ir-A	HOMO-2 5d (%)	HOMO-1 5d (%)	HOMO 5d (%)	LUMO 5d (%)	LUMO+1 5d (%)	LUMO+2 5d (%)
Ir(ppz)$_2$(acac)	2.017 2.039 2.191	0.3%	37.1%	49.9%	2.7%	2.1%	2.1%
Ir(dppzc)($PPhMe_2$)$_2$ (H)(Cl)	2.040 Å 2.155 Å 2.590 Å	13.4%	49.2%	44.8%	2.9%	1.9%	21.18%
Ir(dppzc)($PPhMe_2$)$_2$ (H)(CN)	2.101 Å 2.170 Å 2.040 Å	31.4%	68.3%	39.7%	2.6%	2.1%	21.3%

Table 2. The calculated excitation energies, dominant orbital excitation and oscillator strengths obtained from TD-DFT calculations for Iridium(III) complexes.

	Singlet				Triplet		
	Dominant Excitation	Energy (eV)	Wave length (nm)	Oscillatr Strengths	Dominant Excitation	Energy (eV)	Wave length (nm)
$Ir(dfppy)_2$ (acac)	132→134	2.95	420.4	0.0333	132→134	2.69	460.3
	132→133	2.98	415.5	0.0006	132→133	2.70	458.4
	131→133	3.33	372.8	0.0338	131→136	2.96	418.5
	131→134	3.37	368.3	0.0020	131→134	3.00	412.6
	132→136	3.50	354.3	0.0016	131→133	3.03	409.3
	132→135	3.57	347.4	0.0176	131→134	3.28	378.4
	132→137	3.66	339.0	0.0003	131→133	3.30	375.9
	130→134	3.74	331.4	0.0702	132→135	3.38	367.3
	130→133	3.78	328.2	0.0128	132→136	3.44	360.1
	131→135	3.90	317.8	0.0038	132→137	3.45	359.8
FIrpic	137→139	2.99	415.3	0.0062	137→139	2.73	454.5
	137→138	2.99	414.6	0.0263	137→140	2.78	445.7
	137→140	3.11	398.2	0.0065	137→138	2.95	420.5
	136→139	3.41	363.7	0.0001	136→140	3.07	404.3
	136→138	3.42	362.4	0.0153	134→136	3.10	399.6
	137→141	3.47	357.6	0.0041	136→138	3.17	391.5
	136→140	3.62	342.4	0.0427	136→139	3.35	369.7
	133→138	3.64	340.6	0.0215	137→141	3.36	368.8
	137→142	3.72	333.2	0.0030	133→138	3.37	367.4
	137→143	3.79	327.5	0.0230	135→140	3.40	364.7
Ir(dppzc) $(PPhMe_2)_2$ (H)(Cl)	159→161	3.58	346.6	0.0145	158→162	3.09	401.5
	160→161	3.60	344.1	0.0713	159→161	3.44	360.2
	159→162	3.85	322.4	0.0043	159→161	3.53	351.5
	160→162	3.86	321.2	0.0071	151→165	3.57	347.7
	160→163	4.08	304.2	0.0001	151→166	3.67	338.0
	159→163	4.11	301.9	0.0001	158→162	3.68	337.1
	158→161	4.26	291.2	0.0813	159→161	3.78	328.2
	159→165	4.41	281.2	0.0051	159→161	3.80	326.1
	156→161	4.43	279.6	0.0059	151→165	3.82	324.3
	157→161	4.48	277.1	0.0224	151→166	3.87	320.0
Ir(dppzc) $(PPhMe_2)_2$ (H)(CN)	158→159	3.82	324.8	0.1215	156→160	3.16	392.1
	157→159	3.98	311.8	0.0010	158→159	3.48	356.4
	158→160	4.06	305.2	0.0145	152→162	3.63	341.1
	157→160	4.23	293.1	0.0017	152→161	3.67	338.1
	158→161	4.33	286.2	0.0065	157→159	3.68	337.1
	156→159	4.42	280.7	0.0628	157→159	3.88	319.3
	157→161	4.46	277.9	0.0014	158→160	3.91	317.1
	155→159	4.53	273.6	0.0013	157→159	3.98	311.5
	156→160	4.67	265.8	0.1503	157→160	4.15	298.9
	158→162	4.71	262.9	0.0615	158→166	4.17	297.5

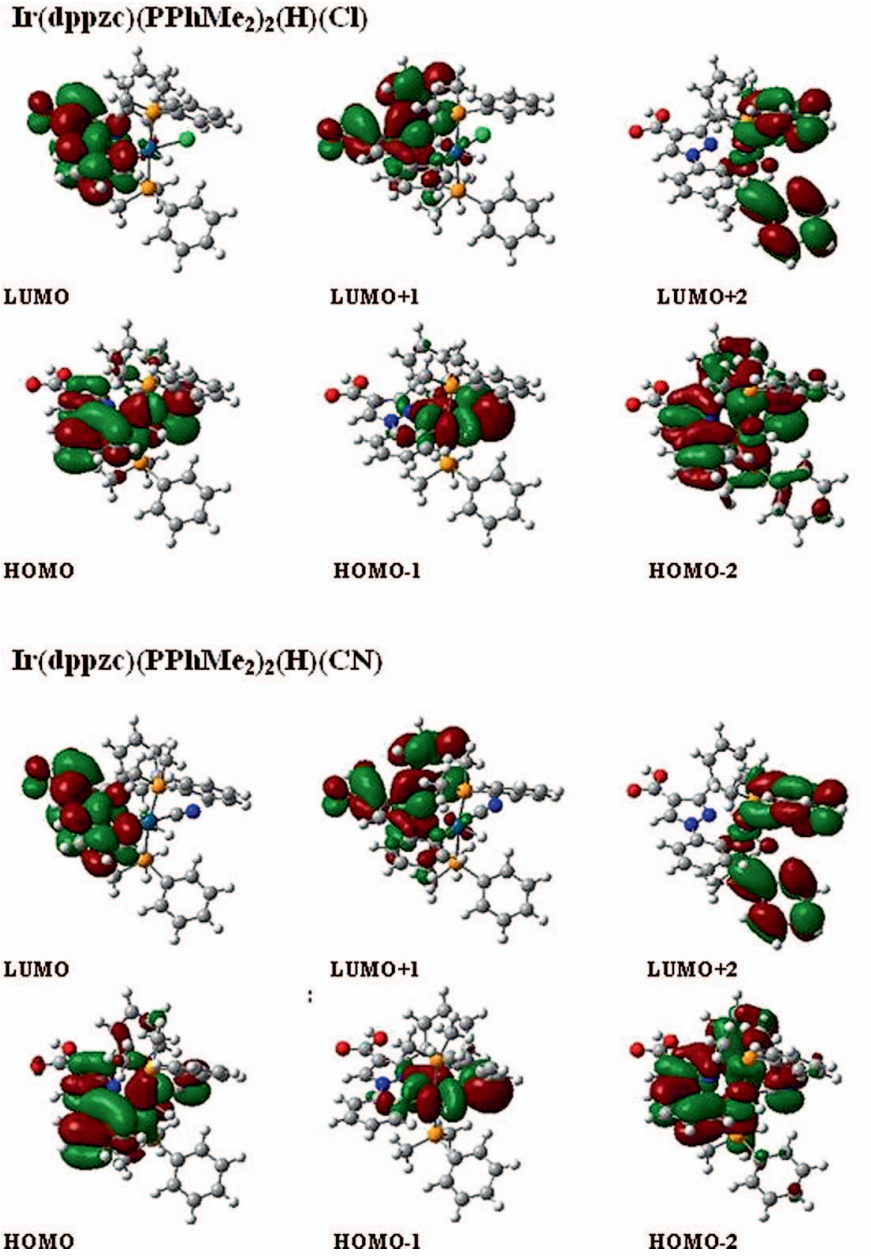

Figure 3. Contour plots of the three highest HOMOs and the three lowest LUMOs of Ir(dppzc)(PPhMe$_2$)$_2$(H)(Cl) and Ir(dppzc)(PPhMe$_2$)$_2$(H)(CN).

It causes red shift by decreasing energy gap. But using the strong-field ancillary ligands such as CN, PPhMe$_2$ is able to increase energy gap. Strong-field ancillary ligands alter the MLCT energy mainly by changing the HOMO energy level. Their inclusion in the coordination sphere can increase the HOMO-LUMO gap to achieve the hypsochromic shift in emission

color and also lower the HOMO & LUMO energy level, which causes significant d-orbital energy splitting and avoids the quenching effect to improve the luminescence efficiency.

As a result, The excitation energy of Ir(dppzc)$(PPhMe_2)_2$(H)(Cl), Ir(dppzc) $(PPhMe_2)_2$(H)-(CN) became greater than that of Ir$(dfppy)_2$(acac) and FIrpic, with a difference of 0.4–0.47 eV, which is a hypsochromic shift of about 53 $\sim$ 68 nm in wavelength. As the maximum emission spectra of FIrpic known as blue phosphorescence material is about 475 nm, we can expect the maximum emission spectra of Ir(dppzc)$(PPhMe_2)_2$(H)(Cl) and Ir(dppzc)$(PPhMe_2)_2$(H)(CN) to be in range of about 425 nm $\sim$ 435 nm.

Conclusions

The ground state and low-lying excited electronic states in the Ir(III) complexes, having one cyclometalating and two phosphines trans to each other and two cis-ancillary ligands, such as Ir(dppzc)$(PPh_2Me)_2$(H)(Cl), Ir(dppzc)$(PPh_2Me)_2$(H)(CN) are studied using density functional. The electronic properties of those molecules are studied using the B3LYP functional and the structure analysis of the optimized geometries is processed in comparison with structures of CˆN ligand and Ir complexes. Excited triplet and singlet states are examined using TD-DFT. The calculated energies of triplets are 3.09 and 3.16 eV, respectively, which are all higher than that of Ir$(dfppy)_2$(acac) and FIrpic known as blue phosphorescence materials with 2.69 and 2.73 eV. Singlets energies of them are 3.58 eV, 3.82 eV, respectively. In this study, we shows that the new type of mixed iridium complex Ir(dppzc)$(PPhMe_2)_2$(H)(Cl) and Ir(dppcz)$(PPhMe_2)_2$ (H)(CN) could expect to act as a good radiation characteristic blue dopant for the fabrication of thermal processing in new phosphorescent OLEDs.

Acknowledgment

This work was supported by 2011 Hongik University Research Funds.

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