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Synthesis, spectroscopic characterization, and molecular structure of triphenyl butene derivatives containing a cyclopentadienyl iron unit

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ABSTRACT

Three hydroxyl substituted triphenyl butene compounds (PHB) and their derivatives containing a cyclopentadienyl iron (PHB-Fc) unit were efficiently synthesized. The synthesis involved the McMurry cross-coupling reaction of appropriate ketones and the nucleophilic aromatic substitution (S_NAr) reaction of (η^6-chlorobenzene) (η^5-cyclopentadienyl) iron hexafluorophosphate (Fc-Cl). The target compounds were characterized by IR, ^1H NMR, ^{13}C NMR, and MS. Their photophysical processes were investigated by UV–Vis absorption and fluorescence emission spectra in acetonitrile. The geometric structure was optimized based on the density functional theory at the B3LYP level. Theoretical results reveal that electron transfer occurred from the HOMO to the LUMO in PHB-Fc. The change in electron distribution subsequently led to the improved second-order optical susceptibility of PHB-Fc.

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1. Introduction

Phenyl conjugated alkene derivatives, such as stilbene and triphenyl butene, have drawn considerable attention in several fundamental studies and applications, including photochemical, biological, and medical activity studies, as well as light and witness applications, photoresponsive materials, and organic electroluminescent materials [1–5]. Phenyl conjugated alkene compounds, which contain a metallic atom in their structures, possess the combined properties of metal and stilbene groups. These compounds produce materials that can be processed with interesting magnetic, electronic, optic, and anisotropic properties [6,7]. Phenyl conjugated alkene derivatives containing the ferrocenyl group has been reported to possess special biological and medical activities. However, reports on the photochemical properties and geometric structure of phenyl conjugated alkene containing cationic cyclopentadienyliron group remain limited [8,9].

Consequently, three hydroxyl substituted triphenyl butene compounds (PHB) and their derivatives containing a cyclopentadienyl iron (PHB-Fc) unit were synthesized in the current study. The relationship between the photochemical properties and structure was investigated. The geometric structures of the triphenylbutene-complexes were optimized, and energy calculations were performed based on the density functional theory (DFT). Given the calculated electronic properties and geometries, the nonlinear second-order optical susceptibility was also calculated.

2. Experimental

2.1. Materials and instruments

All the reagents and solvents in this experiment were of reagent-grade quality, which were obtained from commercial sources and used without further purification. (η^6-Chlorobenzene) (η^5-cyclopentadienyl) iron hexafluorophosphate (Fc-Cl) was prepared through the ligand exchange reaction of ferrocene and chlorobenzene according to the reference procedure [10].

The melting points of the compounds were determined using an XT-4 microscopic melting point apparatus. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV500 unity spectrometer operated at 500 MHz using acetone-d6 as deuterated solvent. FTIR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA). UV–Vis absorption spectra were recorded on a Hitachi U2500 UV–Vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). Mass spectrometry was performed with a Nermag R 10-10C spectrometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrophotometer at room temperature.

A Pentium IV personal computer (CPU at 3.20 GHz) with the Windows XP operating system was used to calculate quantum chemistry. The molecular structures of PHB-FC in the ground state were optimized on the basis of density function theory at the Becke

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3-Lee–Yang–Parr (B3LYP) (Fe with 6-31G** basis set and C, H, and O with Lanl2dz basic set) and by means of visual inspection using the GAUSSVIEW program (Version 5.0). All the calculations were performed using the GAUSSIAN 09 software package.

2.2. Synthesis of triphenyl conjugated butene derivatives

2.2.1. 1-(4-Hydroxyphenyl)-1-phenyl-2-(4-methylphenyl) butylenes (PHB-1)

Propionyl chloride (13.3 g, 0.143 mol) was added dropwise to a stirred solution of $AlCl_3$ (37 g, 0.28 mol) in dry toluene (60 ml) at –5 °C to 0 °C. The mixture was then warmed to room temperature for 1 h and heated to 82 °C for 2 h. The resultant mixture was poured into ice water. The organic layer was washed with 10% Na_2CO_3 as well as saturated NaCl, and then dried over $MgSO_4$. 4-Methyl propiophenone was obtained at 105–110 °C by vacuum distillation (12.6 g, 60.12%).

$TiCl_4$ (3 ml, 0.028 mol) was added dropwise to a stirred suspension of zinc powder (4 g, 0.035 mol) in dry tetrahydrofuran (THF; 40 ml) under N_2 at −10 °C. The reaction mixture was then warmed to room temperature and refluxed for 2 h. A solution of 4-hydroxybenzophenone (1.5 g, 0.0075 mol) and 4-methyl propiophenone (2.2 g, 0.0148 mol) in dry THF (40 ml) was added to the cooled suspension of the titanium reagent at 0 °C. The mixture was refluxed in the dark for 2 h. After being cooled to room temperature, the reaction mixture was quenched with 10% aqueous potassium carbonate (30 ml) and extracted with EtOAc. The organic layer was dried over $MgSO_4$ and concentrated. Flash chromatography afforded PHB-1 (1.53 g, 68%) as a white solid. 4:3 mixture of E/Z isomers, mp: 132–135 °C.

^1H NMR(400 MHz, CH_3COCH_3-d_6) δppm: 0.89–0.93 (t, 3H, J = 7.464 Hz, –$CH_2\mathit{CH}_3$), 2.23 and 2.25 (2 × s, 1H, Ar–CH_3), 2.39–2.45 and 2.46–2.52 (2 × q, 2H, J = 7.45 Hz, –CH_2CH_3), 8.08 and 8.32 (2 × s, 1H, –OH), 6.49–7.37 (m, 13H, 2 × Ar–H); ^{13}C NMR (400 MHz, acetone-d_6): δppm: 8.04 and 8.15 (1C, CH_3), 13.86 and 14.50 (1C, CH_3), 21.01 and 21.11 (1C, CH_2), 115.15 and 115.83 (2C, C_6H_4), 126.39 (2C, C_6H_4), 127.32 (2C, C_6H_5), 128.14 (1C, C), 128.98 (2C, C_6H_4), 130.12 (1C, C_6H_5), 131.29 and 132.58 (2C, C_6H_5), 135.34 (2C, C_6H_4), 136.20 (1C, CH), 139.38 (1C, C_6H_4), 140.33 (1C, C_6H_4), 141.54 (1C, C_6H_4), 144.72 and 145.03 (1C, C_6H_5), 156.30 and 157.12 (1C, C_6H_4); FT-IR spectra $\nu(cm^{-1})$: 3370.1, 3023.3, 2971.1, 2871.9, 1700.3, 1608.51, 1508.8, 1441.7, 1258.5, 1235.9, MS (*m*/*z*): 314.

2.2.2. 1-(4-Hydroxyphenyl)-1-phenyl-2-(4-phenyl) butylenes (PHB-2)

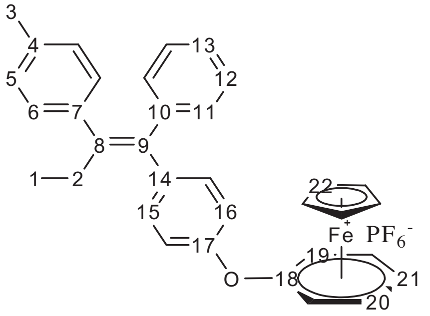
Yield: 57.9%, 4:1 mixture of E/Z isomers, mp: 121–124 °C. ^1H NMR(400 MHz, CH_3COCH_3-d_6) δppm: 0.89–0.92 and 1.18–1.22 (2 × t, 3H, J = 7.43 Hz, –$CH_2\mathit{CH}_3$), 2.41–2.47 (q, 2H, J = 7.43 Hz, –CH_2CH_3), 8.18 and 8.38 (2 × s, 1H, –OH), 6.52–7.40 (m, 14H, 2 × Ar–H); ^{13}C NMR (400 MHz, acetone-d_6): δppm: 8.07 and 8.15 (C, CH_3), 13.81 (1C, CH_2), 115.14 and 115.85 (2C, C_6H_4), 126.77 and 126.87 (2C, C_6H_5), 127.40 and 127.54 (2C, C_6H_4), 128.13 (1C, C_6H_4), 128.62 (2C, C), 130.55 (1C, C_6H_4), 131.30 and 131.41 (1C, C_6H_4), 135.14 and 135.58 (1C, C_6H_5), 143.37 and 143.42 (1C, C_6H_5), 156.35 and 157.18 (1C, C_6H_4); FT-IR spectra $\nu(cm^{-1})$: 3362.2, 2966.9, 1699.1, 1609.6, 1508.4, 1441.3, 1215.54, 1169.9; MS(*m*/*z*): 300.

2.2.3. 1-(4-Hydroxyphenyl)-1-phenyl-2-(4-chlorophenyl) butylenes (PHB-3)

Yield: 62.5%, 7:1 mixture of E/Z isomers, mp: 90–93 °C. ^1H NMR(400 MHz, CH_3COCH_3-d_6) δppm: 0.89–0.92 and 1.18–1.22 (t, 3H, J = 7.45 Hz, –$CH_2\mathit{CH}_3$), 2.42–2.47 and 2.49–2.54 (2 × q, 2H, J = 7.443 Hz, –CH_2CH_3), 8.16 and 8.37 (2 × s, 1H, –OH), 6.52–7.40 (m, 13H, 2 × Ar–H); ^{13}C NMR (400 MHz, acetone-d_6): δppm: 13.75 and 14.50 (1C, CH_3), 20.80 (1C, CH_2), 115.31 and 115.88 (2C, C_6H_4), 127.55 (2C, C_6H_5), 128.71 (1C, C), 129.04 (2C, C_6H_4), 130.02 (2C, C_6H_4), 131.24 and 131.43 (2C, C_6H_5), 132.11 (2C, C_6H_4), 132.30 (1C, C), 132.60 (1C, C_6H_4), 140.43 and 140.53 (1C, C_6H_4), 142.29 (1C, C_6H_4), 144.55 (1C, C_6H_4), 156.58 (1C, C_6H_4); FT-IR spectra $\nu(cm^{-1})$: 3377.1, 2965.5, 1699.7, 1607.3, 1588.9, 1509.6, 1438.7, 1236.8; MS(*m*/*z*): 334.5.

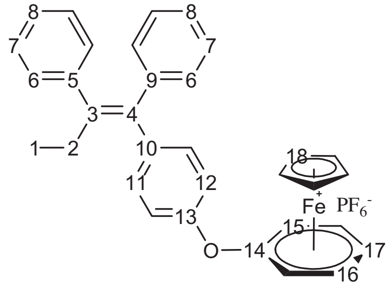
2.2.4. [(η^5-Cyclopentadienyl)-Fe-(η^6-1-(4-phenoxy)-1-phenyl-2-(4-methylphenyl)butylene] hexafluorophosphate (PHB-Fc-1)

The compounds Fc-Cl (0.6 g, 0.0016 mol), PHB-1 (0.5 g, 0.0016 mol), and K_2CO_3 (0.5 g, 0.0.36 mol) were stirred in 40 ml of *N*,*N*-dimethylformamide (DMF) in a 100 ml round bottom flask under a nitrogen atmosphere at 80 °C. Reactions were monitored by thin layer chromatography (TLC) using 0.25 mm aluminum-backed silica gel plates. After Fc-Cl was reacted thoroughly, the reaction mixture was transferred into a 15% (v/v) HCl solution, and a granular precipitate was formed. The obtained filtrate was washed by acetone resulting in the dissolution of the product. This solution was then concentrated by evaporating acetone and treated with sufficient KPF_6 in water to allow for the complete precipitation of PHB-Fcs as a granular solid. The crude product (PHB-Fc-1) was purified by column chromatography and further recrystallized. 4:3 mixture of E/Z isomers, yield: 65.7%, m.p. 172–175 °C.



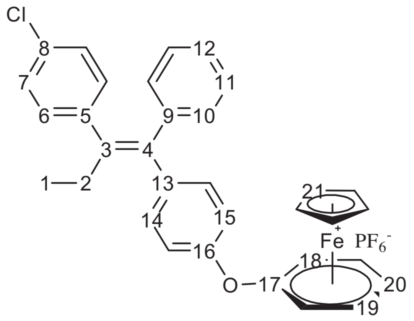
^1H NMR(400 MHz, DMSO-d_6) δppm: 0.85–0.91(t, 3H, J = 7.451 Hz, –$CH_2\mathit{CH}_3$), 2.22 and 2.23(2 × s, 3H, Ar–CH_3), 2.39–2.45(q, 2H, J = 7.455 Hz, –CH_2CH_3), 5.09 and 5.18(2 × s, 5H, arene-Fe-*Cp*), 6.13–6.34(t, 5H, *arene*-Fe-Cp), 6.91–7.44(m, 13H, 2 × Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6): δppm: 13.25 and 13.30 (C_1), 20.65 and 20.69 (C_3), 28.44 (C_2), 76.84 ($5C_{22}$), 84.84 (C_{21}), 86.86 ($2C_{19}$), 120.39 ($2C_{20}$), 125.94 ($2C_{16}$), 126.90 ($2C_{15}$), 127.68 ($2C_6$), 128.50 ($2C_{11}$), 128.95 (C_8), 130.13 (C_{13}), 131.15 ($2C_{12}$), 132.44 ($2C_5$), 135.49 (C_9), 137.02 (C_{14}), 138.22 (C_7), 140.90 (C_4), 142.68 (C_{10}), 150.71 (C_{17}), 151.74 (C_{18}); FT-IR spectra $\nu(cm^{-1})$: 1525.4, 1499.2, 1457.6, 1244.3, 829.6; MS(*m*/*z*): 511 [M-145(PF_6^-)].

2.2.5. [(η^5-Cyclopentadienyl)-Fe-(η^6-1-(4-phenoxy)-1-phenyl-2-(4-phenyl)butylene] hexafluorophosphate (PHB-Fc-2)



Yield: 63.7%, 1:2 mixture of E/Z isomers, m.p. 170–174 °C. ^1H NMR(400 MHz, DMSO-d_6) δppm: 0.87–0.92 (t, 3H, J = 7.166 Hz, –$CH_2\mathit{CH}_3$), 2.40–2.45(q, 2H, J = 7.249 Hz, –CH_2CH_3), 6.12–6.34(t, 5H, *arene*-Fe-Cp), 5.09 and 5.18(2 × s, 5H, arene-Fe-*Cp*), 6.91–7.46(m, 14H, 2 × Ar–H); ^{13}C NMR (400 MHz, DMSO-d$_6$): δppm: 13.20 (C$_1$), 28.32 (C$_2$), 76.83 (5C$_{18}$), 84.68 (2C$_{15}$), 86.86 (C$_{17}$), 86.80 (2C$_{16}$), 119.89 (2C$_{12}$), 120.40 (2C$_{11}$), 126.42 (4C$_6$), 127.64 (C$_3$), 127.93 (2C$_8$), 128.93 (4C$_7$), 129.41 (C$_4$), 137.37 (C$_{10}$), 140.80 (C$_5$), 141.30 (C$_9$), 142.33 (C$_{13}$), 150.73 (C$_{14}$); FT-IR spectra ν(cm^{-1}): 1523.5, 1498.7, 1455.3, 1235.5, 823.6; MS (*m*/*z*): 497[M-145(PF$_6^-$)].

2.2.6. 6[(η^5-Cyclopentadienyl)-Fe-(η^6-1-(4-phenoxy)-1-phenyl-2-(4-chlorophenyl)butylene] hexafluorophosphate(PHB-Fc-3)



Yield: 62.1%, 4:1 mixture of E/Z isomers, m.p. 209–213 °C. ^{1}H NMR(400 MHz, DMSO) δppm: 0.88(s, 3H, –CH$_2$*CH$_3$*), 2.42(s, 2H, –*CH$_2$*CH$_3$), 6.31 and 6.14(2 × s, 5H, arene-Fe-*Cp*), 7.03–7.44(m, 13H, 2 × Ar–H); ^{13}C NMR (400 MHz, DMSO-d$_6$): δppm: 13.13 (C$_1$), 28.11 (C$_2$), 76.82 (5C$_{21}$), 84.75 (2C$_{18}$), 86.68 (C$_{20}$), 87.35 (2C$_{19}$), 120.03 (2C$_{15}$), 127.09 (2C$_{14}$), 127.96 (2C$_{10}$), 128.52 (C$_3$), 128.87 (2C$_6$), 131.00 (C$_{12}$), 131.33 (2C$_{11}$), 132.23 (2C$_7$), 132.50 (C$_4$), 138.09 (C$_{13}$), 140.22 (C$_8$), 140.51 (C$_5$), 141.39 (C$_9$), 142.07 (C$_{16}$), 150.92 (C$_{17}$); FT-IR spectra ν(cm^{-1}): 1522.7, 1497.4, 1455.3, 1233.0, 822.7; MS(*m*/*z*): 531[M-145(PF$_6^-$)].

3. Results and discussion

3.1. Synthesis and characterization

The synthetic pathway and structures of the target compounds are shown in Fig. 1. PHBs were synthesized by the McMurry coupling reaction (Zn and TiCl$_4$), and PHB-Fcs were synthesized by a S$_N$Ar reaction in the presence of potassium carbonate as a base in N,N′-dimethylformamide at 80 °C. The termination of the S$_N$Ar reaction was monitored by observing the disappearance of Fc-Cl via thin-layer chromatography [11,12]. The products were mixtures of *Z* and *E* isomers.

The chemical structures of the derivatives were confirmed by ^{1}H NMR, ^{13}C NMR, IR, and MS, which are detailed in the Experimental section. The optical properties of these target compounds were studied, and isomerization was found to have a minor effect. Consequently, no attempt was made to separate the structures of *Z* and *E* isomers. The mixture of target compounds was synthesized and the ratio of Z/E isomers was confirmed by ^{1}H NMR. The ^{1}H NMR spectrum reveals a single peak at about 8.0 ppm (–OH) or about 5.09 ppm (Cp-Fe). However, the mono peak was divided into two peaks because of the isomerization. The proportion of peaks stands for the ratio of *Z* and *E* isomers.

The IR spectra of PHB-Fcs displayed a strong peak at about 820 cm^{-1} because of the P–F stretching vibration, indicating the existence of PF$_6^-$. In the IR spectra, the ν (O–H) vibration of PHB-Fcs did not exist from 3600 to 3200 cm^{-1}, indicating the disappearance of –OH. The mass spectra showed that the cation was correctly identified.

3.2. Optical properties

Fig. 2 shows the UV–Vis absorption spectra of the compounds in acetonitrile solution. Table 1 summarizes the optical properties of all target compounds. PHB and PHB-Fc had strong and wide absorptions between 200 and 350 nm, which arose from an electron transition process along the entire conjugate system. The

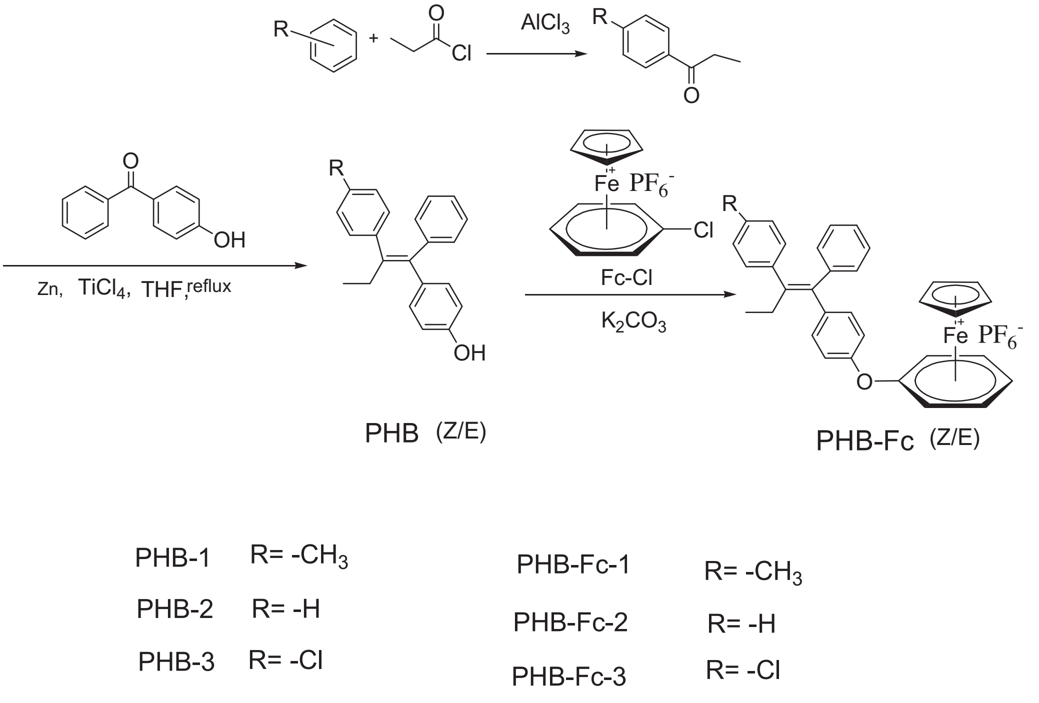


Fig. 1. Synthesis pathway of hydroxyl substituted triphenyl butene compounds (PHB) and their derivatives containing a cyclopentadienyl iron (PHB-Fc) unit.

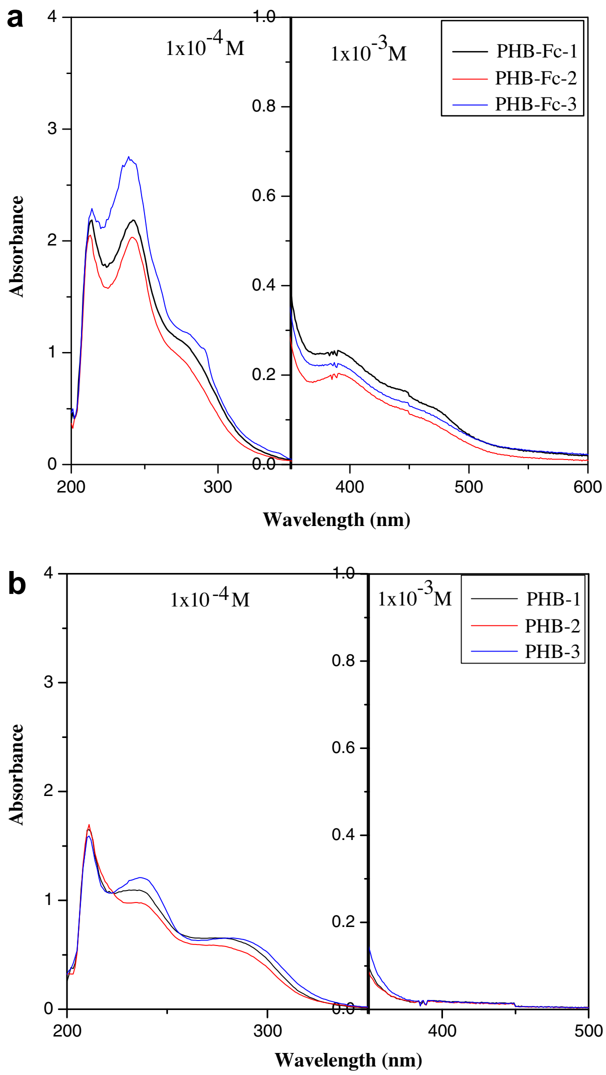


Fig. 2. UV–Vis absorption spectra of PHB-Fc (a) and PHB (a) in acetonitrile.

Table 1
UV–Vis, fluorescent and quantum chemical calculations of the target compounds.

Compound	λ_{max} (nm)[a]	$\times 10$ E^{-4} ε_{max} (L mol^{-1} cm^{-1})[a]	λ_{ex} (nm)[a]	λ_{em} (nm)[a]	Stokes shifts (nm)[b]
PHB-1	212	1.61	277	337	60
PHB-2	210	1.69	278	337	59
PHB-3	210	1.55	275	337	62
	235	1.21			
PHB-Fc-1	213	2.15	302	373	71
	242	2.16			
PHB-Fc-2	213	2.03	305	366	61
	242	2.02			
PHB-Fc-3	214	2.24	293	373	80
	240	2.71			

[a] Solution in 10^{-4} mol L^{-1} CH_3CN.

[b] Stokes shifts = $\lambda_{em} - \lambda_{ex}$.

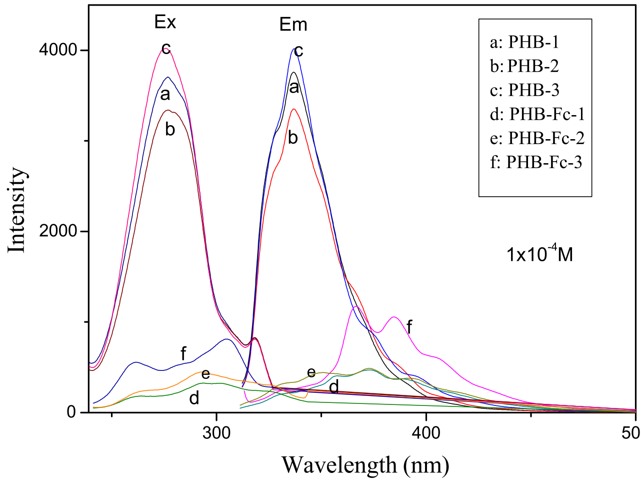


Fig. 3. Fluorescence spectra of PHB and PHB-Fc in CH_3CN.

absorption of PHB-Fc was stronger than that of PHB, and red-shifted to about 50 nm. In contrast, PHB-Fc possesses weak absorption between 400 and 500 nm owing to the d–d transition of the cyclopentadienyl iron unit. Absorption above 400 nm conferred PHB-Fc with photoactivity under visible light. The substituted groups had little effect on the UV–Vis absorption of PHB. PHB-1, PHB-2, and PHB-3 had quite similar absorption characteristics, but PHB-3 had the strongest one because of chloride substitution.

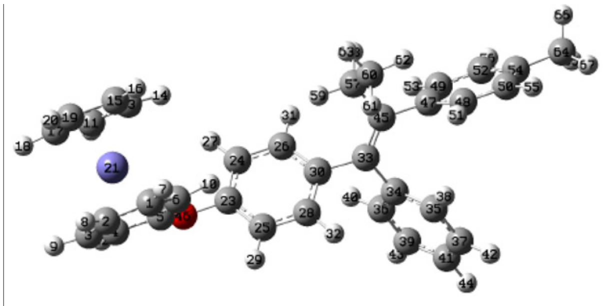
The fluorescence spectra of PHB and PHB-Fc in acetonitrile are shown in Fig. 3. PHB compounds exhibit extremely strong fluorescence. The efficient π-conjugation in PHB constituted by a double bond and three phenyl rings, as well as the rigid structure were responsible for the strong fluorescence. The substituted groups had little effect on the location of the excited and emission peaks of PHB. The emission peak was at 337 nm and the Stokes shift was above 60 nm.

The PHB-Fc compounds exhibited relatively weak fluorescence, a wide fluorescent emission from 330 to 400 nm, and a red-shift at about 40–60 nm compared with PHBs. These characteristics can be attributed to the existence of the electron-withdrawing $[Cp\text{-}Fe]^+$ fragment in PHB-Fc, which could polarize π-electron systems and excite the electron pair on the cyclopentadienyl ring.

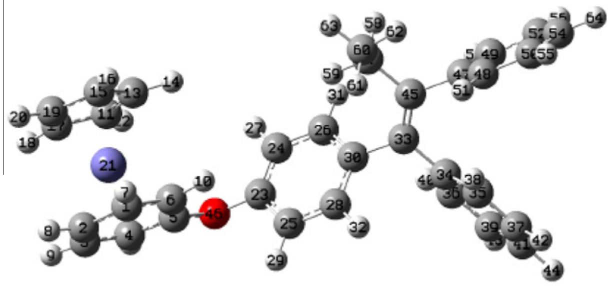
3.3. Quantum chemical calculations

Quantum chemical calculations were used to gain insight into the electronic properties and geometries of PHB and PHB-Fc. The optimized geometries of *E*-PHB-Fcs in the electronic ground state were obtained (Fig. 4). The predicted bond lengths, bond angles and selected dihedral angles for most stable conformer of *E*-PHB-Fc are tabulated in Table 2. As shown in Table 2, bond lengths and valence angles for these new triphenyl conjugated butanes agree with the X-ray crystallographically determined structures that are known for closely related compounds [9b,13,14]. The bond lengths calculated for C=C in E-PHB-Fcs are 1.358 Å, while that in cis-tamoxifen (E) is 1.33 Å and that in trans-tamoxifen (Z) is 1.34 Å at references. The angle formed by the double bond and one of the four substituents is of the order of 122–124° for both the cis- and the trans-tamoxifens at references. In the case of (E)-PHB-Fcs, the bond angles have the following values: C30–C23–C45: 122.9–123.0, C34–C33–C45:113.6–123.5, C33–C45–C57: 121.0–121.2, and C33–C45–C57: 123.6–123.8. It can also be seen that the four substituents on the double bond do not lie in the same plane, the C47–C45–C33–C30 atoms forming a dihedral angle of 3.8–7.9° in the case of *E*-PHB-Fcs. This angle has been found to be 13° for *E*-ferrocenyl tamoxifen which was reported by Siden Top [9b].

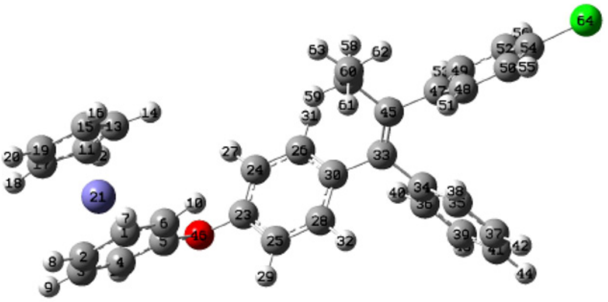
Figs. 5 and 6 show the electron cloud delocalization of the frontier orbitals of the molecules of *E*-PHB and *E*-PHB-Fc, respectively. In the highest occupied molecular orbital (HOMO) and lowest



(*E*)-PHB-Fc-1



(*E*)-PHB-Fc-2



(*E*)-PHB-Fc-3

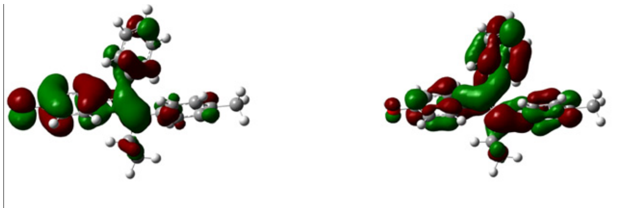
Fig. 4. Optimized geometry of *E*-PHB-Fc on the electronic ground state.

unoccupied molecular orbital (LUMO) of the PHB-Fc compounds, the electron cloud all delocalized over the –C═C– and aryl rings. From HOMO to LUMO, no electron transfer occurred in PHB. In the HOMO of PHB-Fc, the electron cloud delocalized over the –C═C– and aryl rings, whereas in their LUMO orbitals, the electron cloud delocalized over the cyclopentadienyliron cation and coordinated arena. This finding suggested that electron transfer occurred from the HOMO to the LUMO in PHB-Fc.

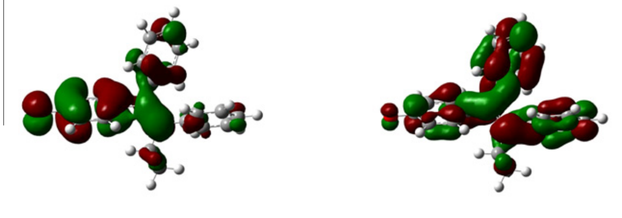
Generally, the energy values of LUMO and HOMO, as well as their energy gaps reflect the chemical activity of a molecule. HOMO as an electron donor represents the ability to donate an electron, and LUMO as an electron acceptor represents the ability to obtain an electron. Smaller LUMO and HOMO energy gaps correspond to an easier excitability the HOMO electrons. The HOMO and LUMO energies of the target compounds based on the optimized structure were computed. Table 3 shows that the HOMO–LUMO energy gaps Δ*E* of PHB-Fc were smaller than those of PHB compounds, and Δ*E* of *E*-isomers were lower than those of *Z*-isomers. These findings were consistent with those of the UV–Vis absorption.

Table 2
Optimized geometrical parameters of PHB-Fc based on B3LYP.

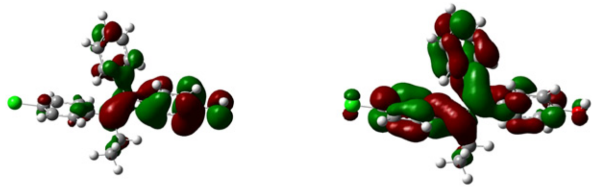
Parameters	PHB-Fc-1	PHB-Fc-2	PHB-Fc-3
Bond lengths (Å)			
C30–C33	1.498	1.498	1.498
C33–C34	1.499	1.499	1.499
C45–C57	1.523	1.522	1.523
C45–C47	1.500	1.501	1.501
C33–C45	1.358	1.358	1.358
Bond angles (°)			
C30–C23–C45	122.96	122.96	123.01
C34–C33–C45	123.47	113.57	113.63
C33–C45–C47	121.19	121.17	121.00
C33–C45–C57	123.65	123.75	123.78
Dihedral angles (°)			
C47–C45–C33–C30	3.894	3.700	3.928
C47–C45–C33–C34	7.945	7.587	7.974



(*E*)-PHB-1 **HOMO** (*E*)-PHB-1 **LUMO**



(*E*)-PHB-2 **HOMO** (*E*)-PHB-2 **LUMO**



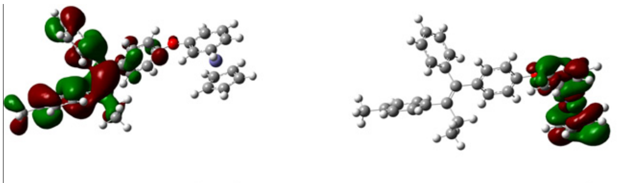
(*E*)-PHB-3 **HOMO** (*E*)-PHB-3 **LUMO**

Fig. 5. Molecular orbital surface and energies of target compounds frontier molecular orbitals of PHB.

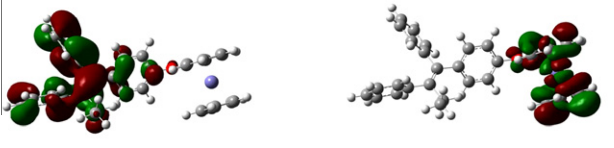
3.4. Static second-order nonlinear optical (NLO) properties

Organometallic and coordination complexes with enhanced NLO properties continue to be in the limelight over the past two decades [15–21]. They exhibit large and fast nonlinearities by introducing new NLO active charge-transfer transitions between the metal and the ligand, such as metal-to-ligand charge transfer and ligand-to-metal charge transfer [22,23]. These advantages of metal complexes are conducive to the efficient switching of second-order NLO responses at the molecular level, which could provide the basis for a range of molecular-scale devices.

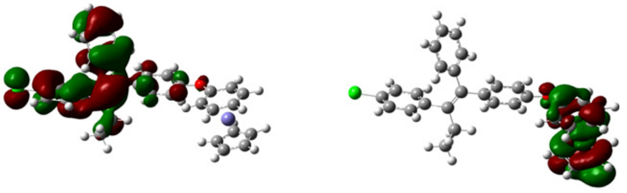
Theoretical investigations play an important role in understanding structure–property relationships, which can assist in designing novel NLO materials. In the PHB-Fc compounds, the



(*E*)-PHB-Fc-1 HOMO **(*E*)-PHB-Fc-1 LUMO**



(*E*)-PHB-Fc-2HOMO **(*E*)-PHB-Fc-2 LUMO**



(*E*)-PHB-Fc-3 HOMO **(*E*)-PHB-Fc-1 LUMO**

Fig. 6. Molecular orbital surface and energies of target compounds frontier molecular orbitals of *E*-PHB-Fc.

Table 3
Caculated values of the electrostatic first hyperpolarizability.

Compound	E_{Homo} (eV)	E_{Lumo} (eV)	ΔE (eV)[a]	$\beta \times 10^{-30}$ *esu*
PHB-1	$(E) - 13.417$	-2.542	9.564	0.885
PHB-2	$(E) - 12.126$	-2.566	9.560	0.937
PHB-3	$(E){-}11.677$	-2.500	9.177	2.122
PHB-Fc-1	$(E) - 7.705$	-5.577	2.128	7.561
PHB-Fc-2	$(E) - 7.726$	-5.174	2.552	6.997
PHB-Fc-3	$(E) - 7.788$	-5.220	2.568	11.282

[a] $\Delta E = (E_{\mathrm{Lumo}} - E_{\mathrm{Homo}})$.

coordination of ligand groups to metal centers could generate push–pull systems. The enhancement of charge separation is known to favor large NLO responses [24]. Consequently, the electrostatic first hyperpolarizability (β) was calculated using the GAUSSIAN 09 package.

Based on the calculated electronic properties and geometries, the electrostatic first hyperpolarizability β_{ijk} and β_μ were calculated using the DFT/B3LYP method. The components of β are defined as the coefficients in the Taylor series expansion of the external electric field energy. Using x, y, and z components, the electrostatic first hyperpolarizability β_μ is defined as:

$$\beta_\mu = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

and

$$\beta_j = \beta_{jjj} + \frac{1}{3}\sum_{i \neq j}(\beta_{jii} + 2\beta_{ijj}) \qquad (i \neq j; i, j = x, y, z)$$

The β_μ of the title compounds are shown in Table 3. The second-order optical susceptibility of the target compounds followed the order: β_μ (PHB) < β_μ (PHB-Fc) and β_μ (Z) < β_μ (E). This trend is attributed to the intermolecular charge-transfer of the PHB-Fc compounds. The electron-rich triphenylethylene group became the donor, and the $[\mathrm{Cp\text{-}Fe}]^+$ fragment became the acceptor. This switching of electron distribution directly affected the NLO coefficient, which could generate push–pull systems. Such systems favor the generation of large NLO responses.

4. Conclusion

Three stilbene compounds (PHB) and their derivatives containing a cyclopentadienyl iron (PHB-Fc) unit were successfully synthesized and characterized. UV–Vis absorption and fluorescence emission spectrum analyses showed that introducing the cyclopentadienyl iron unit strengthened the UV–Vis absorption of PHB-Fc and weakened the fluorescence emission compared with those of PHB. The optimized molecular structures and energy levels of frontier molecular orbitals were obtained on the basis of DFT at the B3PW91/Lanl2dz level. The cyclopentadienyl iron unit was found to be a strong electron-withdrawing group. Electron transfer occurred from the HOMO to the LUMO in PHB-Fc. The change in electron distribution subsequently led to the improved second-order optical susceptibility of PHB-Fc.

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