Electronic Supplementary Information

Ferrocene-quinoxaline Y-shaped chromophores as fascinating second-order NLO building blocks for long lasting highly active SHG polymeric films

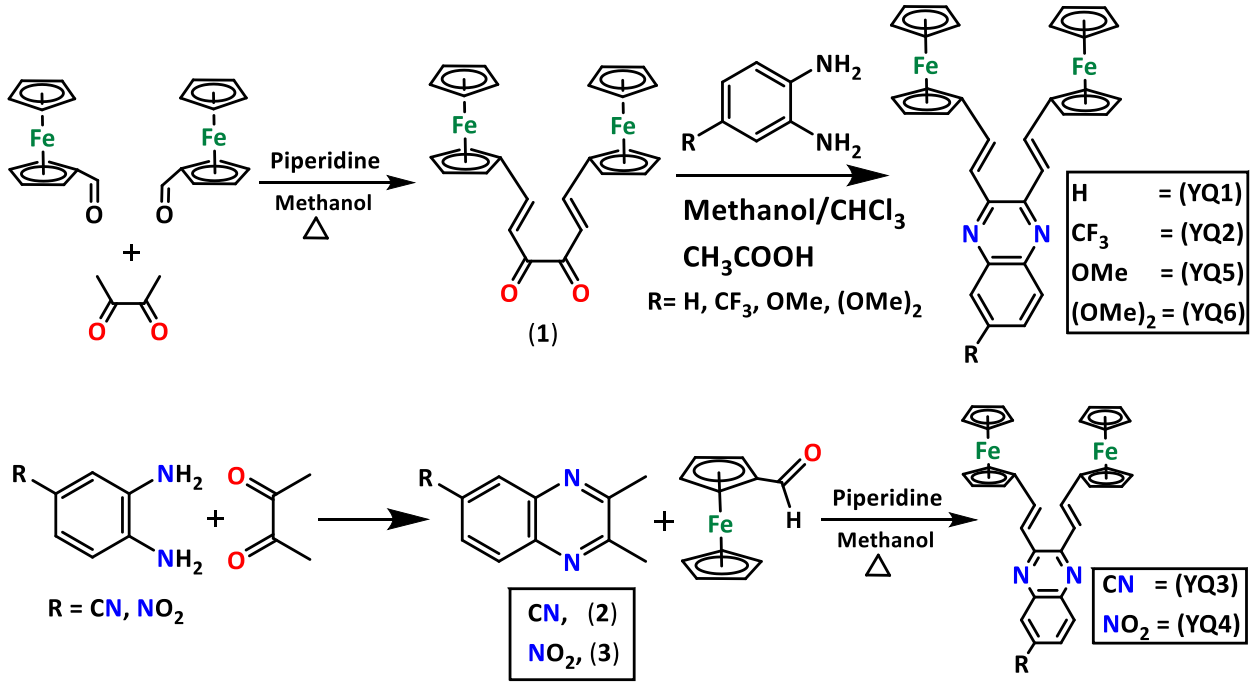
Kabali Senthilkumar,[a] Krishnan Thirumoorthy,[a] Claudia Dragonetti,[b,c] Daniele Marinotto,[b] Stefania Righetto,[b] Alessia Colombo,[b*] Matti Haukka,[d] Nallasamy Palanisami[a*]

a. Department of Chemistry, School of Advanced Sciences, VIT University, Vellore 632014, Tamilnadu, India.

b. Department of Chemistry and Centro CIMAINA, University of Milan, INSTM-Research Unit, Via C. Golgi 19, 20133 Milan, Italy.

c. ISTM-CNR via Golgi 19 Milan, Italy

d. Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland.



Scheme 1. Synthetic routes for different substituted Y-shaped quinoxaline chromophores (**YQ1-6**)

EXPERIMENTAL

Materials and Procedures

The (1*E*,5*E*)-1,6-Bisferrocenyl-hexa-1,5-diene-3,4-dione (**1**) were synthesized from reported procedure.[1,2] Products were dried overnight in a vacuum desiccator ($CaCl_2$) before to be characterized. Chromatographic separations were carried out using silica gel 60 (AVRA, 100 − 120 mesh). Other solvents were of reagent grade and were used without further purification. All other chemicals were purchased from M/s. Aldrich Chemical Co. And M/s. Johnson Matthey Chemicals. The condensation of an (1E,5E)-1,6-Bisferrocenyl-hexa-1,5-diene-3,4-dione (**1**) with an substituted 1,2-diamine (R= H, CF_3, OMe and (OMe_2)) is one of the most versatile methods used for the construction of quinoxaline derivatives **YQ1**, **YQ2**, **YQ5**, **YQ6** as shown in scheme 1. Remaining derivatives **YQ3** and **YQ4** are synthesized by different synthetic strategy as shown in the scheme 1. Starting from the corresponding derivatives **2-4** (synthesized by condensation

reaction of cyano and nitro substituted 1,2-diamine and 2,3-butadione) and ferrocenecarboxaldehyde in the presence of piperidine and methanol as solvent, the target compounds **YQ3** and **YQ4** were prepared through a Knoevenagel condensation.

General Physical Measurements

The NMR spectra were recorded on a BRUKER (400 MHz) spectrometer. Chemical shifts are reported in δ (ppm) and mass spectra were recorded on a Q-Tof-Mass Spectometer and JEOL-AccuTOF JMS-T100LC mass spectrometer (Jeol, Tokyo, Japan) fitted with a DART ion source. Micro elemental analyses were determined by PERKIN-ELMER CHN-2400. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70 attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrometer. All UV–visible absorption spectra were recorded on a Varian Cary Bio UV 100 UV–visible spectrophotometer in a 1 cm^2 quartz cuvette at room temperature using CH_2Cl_2 solvent. The films thickness was determined using a Bruker DektakXT profilometer. The SEM images were recorded with an Hitachi TM-1000 Tabletop Microscope.

Single-crystal X-ray structure determination of chromophores (YQ1 and YQ2)

All crystals were obtained by a slow evaporation of the corresponding solutions (CH_2Cl_2 and MeOH) at room temperature. Crystals were stored in paraffin-oil and mounted in a MiTeGenloop, and measured at 100 to 120 K. The crystal approximate dimensions are 0.25 x 0.05 x 0.03 mm^3 (for **YQ1**), 0.30 x 0.30 x 0.25 mm^3 (for **YQ2**). The X-ray diffraction data were collected on a Agilent SuperNova (Oxford Diffraction) diffractometer using Mo-K_α radiation (λ=0.71073 Å) for **YQ1** and Bruker axs kappa apex2 CCD Diffractometer using Mo-K_α radiation (λ=0.71073 Å) for **YQ2**. The Apex2[3] package was used for cell refinements and data reductions. The structures were solved by direct methods using the Shelxs 97[4] or Superflip[5] program with

the Olex 2[6] graphical user interface. Structural refinements were carried out using Shelxl-97 or Shelxl-2014.[4,7]

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C − H = 0.95 − 0.1.00 Å, and U_{iso} = 1.2 − 1.5U_{eq} (parent atom). The crystallographic details are summarized in Table S1.

EFISH measurements

All of the EFISH measurements[8] were carried out in $CHCl_3$ solutions at 10^{-3} M concentration, with a non-resonant incident wavelength of 1.907 µm, obtained by Raman-shifting the fundamental 1.064 µm wavelength produced by a Q-switched, mode-locked Nd^{3+}:YAG laser manufactured by Atalaser. The apparatus used for EFISH measurements is a prototype made by SOPRA (France). The $\mu\beta_{EFISH}$ values reported are the mean values of 16 measurements performed on the same sample. The sign of $\mu\beta$ is determined by comparison with the solvent ($CHCl_3$). All measurements are negative, this means that $\Delta\mu_{eg}$ is negative (e=excited, g= ground state).

Preparation of thin films of chromophores in PMMA and polystyrene related SHG measurements

Composite films were produced by spin coating on ordinary non-pretreated glass substrates (thickness 1 mm) previously cleaned with water/acetone. The solution was obtained from 300 mg of polymer, polymethylmethacrylate (PMMA) or polystyrene (PS) and 15 mg of **YQ2** dissolved in dichloromethane (4.5 mL). Parameters of spinning (RPM revolutions per minute) RPM 1:500; Ramp 1:1 s, Time 1:3 s; RPM 2:1500; Ramp 2:4 s, Time 2:25 s; RPM 3:2000; Ramp 3:1 s, Time 3:1 s. The film thickness of composite PMMA (or) polystyrene/**YQ2** was

measured by the profilometer. Second Harmonic Generation (SHG) experiments were performed using a Q-switched Nd:YAG (Quanta System Giant G790-20) laser at 1.064 μm wavelength with a pulse of 7 ns and 20 Hz repetition rate. For poling measurements, the fundamental beam was attenuated to 0.57 m*J* and was focused with a lens (f = 600 mm) on the sample, placed over the hot stage. The corona poling process was carried out inside a specially built dry box, in N_2 atmosphere. The fundamental beam was polarized in the plane of incidence (p-polarized) with an angle of about 55˚ with respect to the sample in order to optimize the SHG signal. The hot stage temperature was controlled by a GEFRAN 800 controller, while the corona wire voltage (up to 10.0 kV across a 10 mm gap) was applied by a TREK610E high-voltage-supply. After rejection of the fundamental beam by an interference filter and a glass cut-off filter, the p-polarized SHG signal at 532 nm was detected with a UV-Vis photomultiplier (PT) Hamamatsu C3830.[9–14]

The corona wire poling dynamics of the SHG behavior of polystyrene and PMMA composite film was performed using the following parameters: temperature and electric field, of 75 °C and 10 kV for complex **YQ2**/polystyrene film and 65 °C and 9.5 kV for complex YQ2/PMMA film; these conditions allowed us to obtain a sufficiently high and stable second-harmonic generation (SHG) signal. The absorption bands of **YQ2** in polystyrene and in PMMA films (peaks at 356 nm and 522nm) after poling (blue line) decrease compared to that observed before poling (black line). It's the "so-called" dichroic effect[15] due to the partial orientation of molecules along the direction of the electric poling field. No appreciable Stark shift[15] of the absorption peaks was noted after poling as shown in Fig. S1.

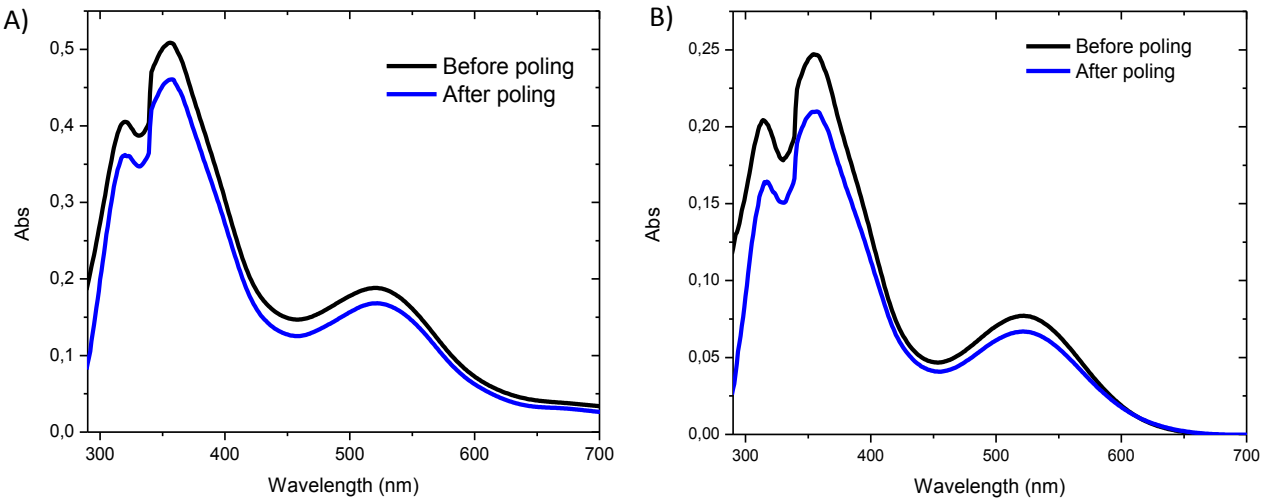


Figure S1: UV/Vis absorption spectra of **YQ2** in A) polystyrene and B) PMMA matrix after and before poling.

Method of calculation of the d_{33} values

In the Maker fringe experiment, the second harmonic (SH) intensity was detected as a function of the incidence angle θ of the fundamental beam and normalized with respect to that of a calibrated quartz crystal wafer (X-cut) 1 mm thick whose d_{11} is 0.46 pm/V. The incidence angle was changed by rotating the poled film along the Y axis (see Fig. S2) while the polarization of the fundamental and SH beam could be changed by a half-wave plate and a cube beam splitter respectively.

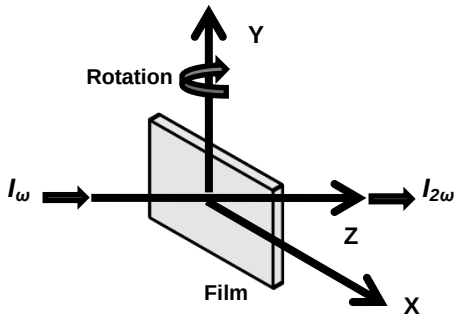


Figure S2: Maker Fringe. (XYZ is the macroscopic coordinate system).

In order to determine the nonzero independent components of the susceptibility tensor for poled films ($C_{\infty v}$ symmetry) Maker fringe measurements were conducted with the following polarizations: p→p, s→p and 45→s. The standard expression[13] used to fit the SHG intensity in a Maker fringe measurement includes the absorption coefficient of the film at the harmonic frequency. In this expression the SHG intensity is proportional to the square of the effective nonlinear optical coefficient (d_{eff}) which depends on polarizations of the fundamental and SH beam. Considering the $C_{\infty v}$ symmetry expected for poled films and the polarizations of the fundamental and SH beam, the coefficient d_{eff} assumes the following expression:

$$d_{eff} = d_{ZXX} \sin \vartheta_2 \qquad (1a)$$

for s→p configuration,

$$d_{eff} = d_{XXZ} \sin \vartheta_1 \qquad (1b)$$

for 45→s configuration,

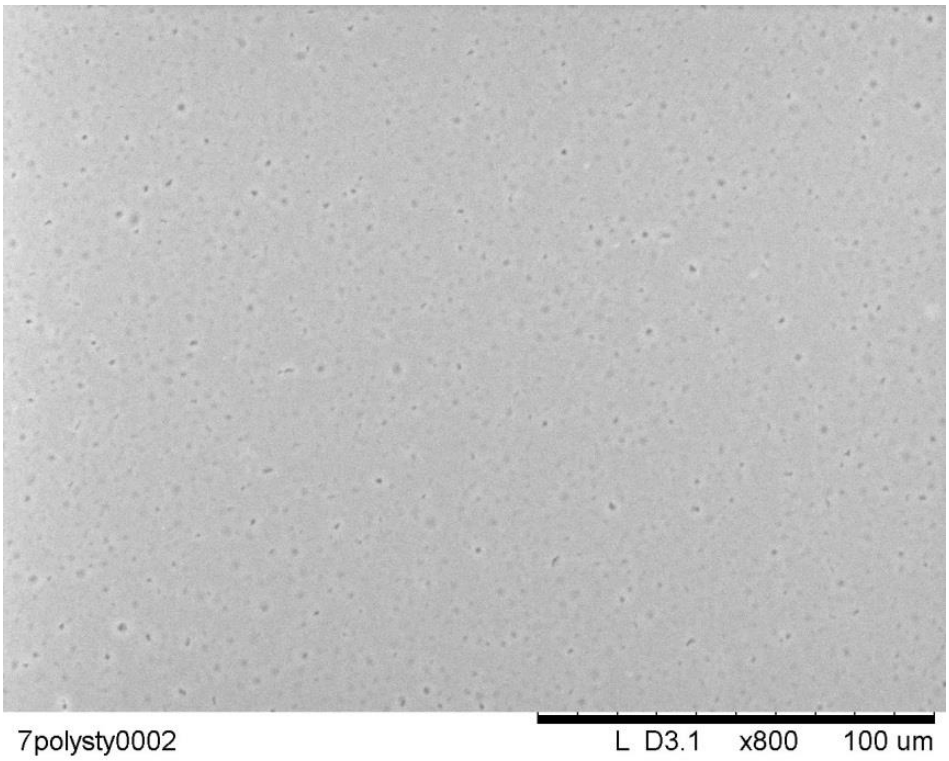
$$d_{eff} = 2d_{XXZ} \sin \vartheta_1 \cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_2 \left(d_{ZXX} \cos^2 \vartheta_1 + d_{ZZZ} \sin^2 \vartheta_1 \right) \qquad (1c)$$

for p→p configuration, where θ_1 and θ_2 are respectively the angles of refraction inside the poled film for the fundamental and SH beam with refractive indices n_ω and $n_{2\omega}$ ($\sin\theta_m = \sin\theta / n_{m\omega}$, m=1,2).

Morphological investigations by SEM measurements

Thin films morphology was analysed by scanning electron microscopy (SEM) covering a large area of the samples. The composite films seem to consist in smooth basal layers with few small droplets randomly distributed on the surface but overall the films (in particular B) are compact and uniformly grown (see Fig. S3).

A)



B)

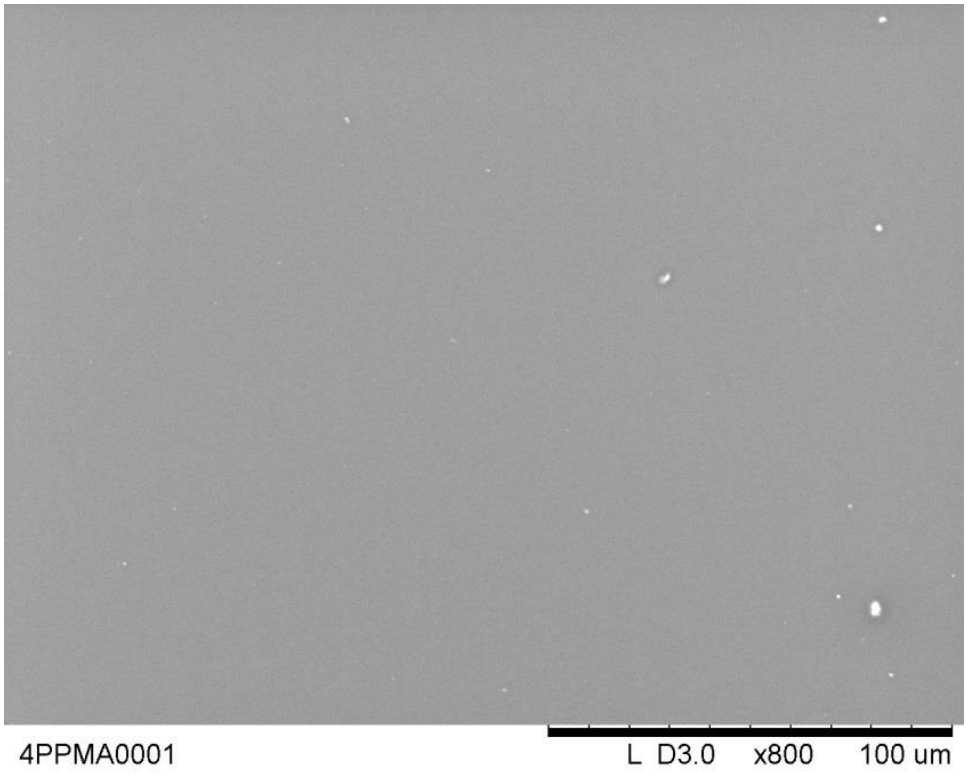


Figure S3. SEM image of A) Polystyrene and B) PMMA thin films.

Theoretical Calculations

The electronic structures and molecular properties of Y shaped quinoxaline chromophores were investigated using density functional theory (DFT) to understand bonding patterns, the electronic charge and molecular orbital energy distributions. The initial geometry of chromophore was taken from the available crystal data for **YQ1** and **YQ2.** The guess structures of remaining chromophores were obtained by replacing the substitution in the phenyl ring corresponding position in **YQ1**. The geometries of synthesized chromophores in the gas phase were optimized using Becke's three-parameter and Lee-Yang-Parr functional as B3LYP.[16–18] The DFT/B3LYP level of computational calculations were carried out using 6-31+G** basis set for finding the global minimum energy structure of all chromophores and its molecular properties calculations. Inclusion of diffusion and polarization functions in 6-31+G** basis set accounts the electronic charge distributions and effects of polarization in atomic orbitals in all quinoxaline chromophores. In addition, time-dependent density functional (TD-DFT) theoretical method was utilized for finding the molecular orbital energy distributions within the first 20 excited singlet states. On the optimized gas phase geometries, TD-DFT studies have been carried out with B3LYP/6-31+G** method, both in *vacuo* and in CH_2Cl_2 using PCM model of solvation method. All computation calculations were performed using the G09 package.[19] Electronic geometries, frontier molecular orbital structures were taken using GaussView 5[20] molecular visualization program.

Synthesis of quinoxaline Derivatives (YQ1, YQ2, YQ5 and YQ6)

Solution of **1** (0.478 g, 1 mmol) in chloroform was added to a methanolic solution of diamine (1 mmol) and followed by acetic acid (0.5 mL) was added and the reaction mixture was refluxed overnight. The completion of the reaction was monitored through thin layer chromatography.

The solvent was removed in a rotary evaporator and the residue was poured in water and separated with chloroform and solvent was removed. The crude product was purified through silica gel thin layer chromatography using ethyl acetate/hexane as the eluent.

2,3-bis((*E*)-2-ferrocenylstyryl)-quinoxaline (**YQ1**)

o-Phenylenediamine, (0.108 g, 1 mmol), yield 84 %. mp = 198 ˚C. $C_{32}H_{26}Fe_2N_2$: calcd. C, 69.85; H, 4.76; N, 5.09; found C, 69.32; H, 4.81; N, 5.78 %. TOF MS (ESI): *m/z* (M^+) = 550. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (dd, *J* = 6.3, 3.5 Hz, 2H), 7.74 (d, *J* = 15.3 Hz, 2H), 7.62 – 7.53 (t, 2H), 7.13 (d, *J* = 15.3 Hz, 2H), 4.57 (t, *J* = 1.9 Hz, 4H), 4.36 (t, *J* = 1.9 Hz, 4H), 4.15 (s, 10H) ppm. FTIR: 3074(m), 3051(m), 2962(s), 1616(s), 1512(s), 1400(s), 1303(s), 1261(s), 1199(s), 1099(s), 958(s), 800(s), 756(s), 609(s), 474(s) cm^{-1}.

2,3-bis((*E*)-2-ferrocenylstyryl)-6-(trifluoromethyl)quinoxaline (**YQ2**)

4-(trifluoromethyl)benzene-1,2-diamine, (0.176 g, 1 mmol), yield 81%. mp = 206 ˚C. $C_{33}H_{25}F_3Fe_2N_2$: calcd. C, 64.11; H, 4.08; N, 4.53; found C, 63.98; H, 4.01; N, 4.28 %. TOF MS (ESI): *m/z* (M^+) = 618. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.23 (s, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.82 (d, *J* = 15.3 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 15.3 Hz, 2H), 4.59 – 4.54 (s, 4H), 4.38 (s, 4H), 4.14 (s, 10H) ppm. ^{19}F NMR (377 MHz, Chloroform-d): δ –62.46 (s, -CF_3) ppm. FTIR: 3089(m), 2920(s), 2846(m), 1616(s), 1514(s), 1404(m), 1284(s), 1191(s), 1155(m), 1105(s), 1055(s), 956(s), 893(m), 810(s), 692(m), 576(m), 511(s), 480(s) cm^{-1}.

2,3-bis((*E*)-2-ferrocenylstyryl)-6-methoxyquinoxaline (**YQ5**)

4-methoxybenzene-1,2-diamine, (0.138 g, 1 mmol), yield 86%. mp = 285 ˚C. $C_{33}H_{28}Fe_2N_2O$: calcd. C, 68.30; H, 4.86; N, 4.83; found C, 68.14; H, 4.75; N, 4.76 %. TOF MS (ESI): *m/z* (M^+) = 581.4. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.72 (s, 1H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.62 (d, *J* =

15.4 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 14.6 Hz, 2H), 4.58 (t, 4H), 4.37 (t, 4H), 4.15 (s, 10H), 3.91 (s, 1H) ppm. FTIR: 3072(m), 2962(s), 2920(m), 2846(m), 1733(m), 1612(s), 1517(m), 1489(s), 1438(m), 1313(m), 1261(s), 1215(s), 1101(s), 1024(s), 962(s), 798(s), 748(s), 611(s), 520(s), 480(s), 420(s) cm^{-1}.

2,3-bis((*E*)-2-ferrocenylstyryl)- 6,7-dimethoxyquinoxaline (**YQ6**)

4,5-dimethoxybenzene-1,2-diamine, (0.168 g, 1 mmol), yield 74%. mp = >300˚C. $C_{34}H_{30}Fe_2N_2O_2$: calcd. C, 66.91; H, 4.95; N, 4.59; found C, 66.71; H, 4.34; N, 4.86 %. TOF MS (ESI): *m/z* (M^+) = 611.4. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 (d, *J* = 15.4 Hz, 2H), 7.23 (s, 2H), 7.12 (d, *J* = 15.4 Hz, 2H), 4.55 (t, *J* = 1.9 Hz, 4H), 4.33 (t, *J* = 1.9 Hz, 4H), 4.14 (s, 10H), 4.00 (s, 6H) ppm. FTIR: 3078(m), 3001(m), 2952(m), 2827(m), 1620(s), 1492(s), 1429(m), 1307(s), 1218(s), 1166(s), 1105(m), 1018(m), 970(m), 817(m), 615(s), 499(s), 480(s), 437(m) cm^{-1}.

2,3-dimethyl-6-cyanoquinoxaline (2) and 2,3-dimethyl-6-nitroquinoxaline (3)

A mixture of 4-nitrobenzene-1,2-diamine/3,4-diaminobenzonitrile (1 mmol), 2,3-butadione (1 mmol) and absolute ethanol/acetic acid (5 ml/0.5 ml) was refluxed until completion of the reaction. The reaction was monitored by thin layer chromatography. After the reaction was completed the mixture was poured into the water, precipated products was filtered and dried. The pure product was afforded by recrystallization. **2**; MS (EI): *m/z* (M^+) = 183.31. **3**; MS (EI): *m/z* (M^+) = 203.20.

2,3-bis((*E*)-2-ferrocenylstyryl)-6-cyanoquinoxaline (**YQ4**)

A mixture of **2** (0.091 g, 0.5 mmol), FcCHO (0.214g, 1 mmol) and a small portion of piperidine in anhydrous toluene (10 ml) was refluxed under a N_2 atmosphere. The reaction was confirmed using thin layer chromatography. After cooling to room temperature, the remaining liquid was

concentrated and purified by column chromatography on silica gel using hexane/ethylacetate (9:1) as eluent to produce a solid product. yield 74%. mp = 197 ˚C. $C_{33}H_{25}Fe_2N_3$: calcd. C, 68.90; H, 4.38; N, 7.30; found C, 68.86; H, 4.27; N, 7.63 %. TOF MS (ESI): *m/z* (M^+) = 576.68. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.27 (s, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 15.2 Hz, 2H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 4.59 (t, 4H), 4.44 (t, 4H), 4.16 (s, 10H) ppm. FTIR: 3074(m), 2918(s), 2848(m), 2225(s), 1679(s), 1620(s), 1541(s), 1398(s), 1375(m), 132(m), 1241(m), 1120(m), 1105(m), 999(m), 960(s), 908(m), 812(m), 634(m), 613(s), 497(s), 478(s) cm^{-1}.

2,3-bis((*E*)-2-ferrocenylstyryl)-6-nitroquinoxaline (**YQ3**)

A mixture of **3** (0.102 g, 0.5 mmol), FcCHO (0.214 g, 1 mmol) and a small portion of piperidine in anhydrous toluene (10 ml) was refluxed under a N_2 atmosphere. The reaction was confirmed using thin layer chromatography. After cooling to room temperature, the remaining liquid was concentrated and purified by column chromatography on silica gel using hexane/ethylacetate (9:1) as eluent to produce a solid product. Yield 74%. mp = 208-210 ˚C. $C_{32}H_{25}Fe_2N_3O_2$: calcd. C, 64.57; H, 4.23; N, 7.06; found C, 64.19; H, 4.42; N, 7.61 %. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.76 (d, *J* = 2.6 Hz, 1H), 8.34 (d, *J* = 2.6 Hz, 1H), 8.01 (d, *J* = 4.3 Hz, 2H), 7.97 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 15.2 Hz, 2H), 4.58 (s, 4H), 4.43 (s, 4H), 4.15 (s, 10H) ppm. FTIR: 3089(m), 2922(m), 2848(w), 1679(s), 1616(s), 1517(s), 1398(s), 1330(s), 1244(s), 1105(s), 1001(s), 960(s), 902(s), 815(s), 738(s), 702(s), 621(s), 478(s) cm^{-1}.

Table S1. Crystallographic data and structure refinement details for **YQ1** and **YQ2**.

Identification code	**YQ1**	**YQ2**
CCDC	1440374	1440375
Empirical formula	$C_{32}H_{26}Fe_2N_2$	$C_{33}H_{25}F_3Fe_2N_2$
Formula weight	550.25	618.25
Temperature, K	120(2)	293(2)
Wavelength, Å	1.54184	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a, Å	a = 5.88(11)	a =7.35(11)
b, Å	b = 17.93(4)	b = 11.91(17)
c, Å	c = 22.87(4)	c = 15.84(2)
a, °	90	82.43(8)
b, °	94.53	80.52(8)
g, °	90	73.27(8)
Volume $Å^3$	2405.58(8)	1306.6(3)
Z	4	2
Density (calculated) Mg/m^3	1.519	1.571
Absorption coefficient mm^{-1}	9.850	1.159
F(000)	1136	632
Crystal size mm^3	0.25 x 0.05 x 0.03	0.30 x 0.30 x 0.25
Theta range for data collection	3.134 to 77.057	1.308 to 24.345
Reflections collected	32178	20285
Data / restraints / parameters	5084 / 0 / 325	20285 / 159 / 391
Goodness-of-fit on F^2	1.016	1.083
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0469$, $wR_2 = 0.1255$	$R_1 = 0.1099$, $wR_2 = 0.2791$
R indices (all data)	$R_1 = 0.0502$, $wR_2 = 0.1292$	$R_1 = 0.1494$, $wR_2 = 0.3022$

Table S2. Important geometrical parameters for crystal structure of **YQ1** and **YQ2**. The interatomic distances are reported in Å, angels in degrees.

	YQ1	**YQ2**
Average Fe(1)-C	2.056(4)	2.045(4)
Average Fe(2)-C	2.047(8)	2.017(7)
Fe(1)-Cent(1)	1.662(4)	1.644(3)
Fe(1)-Cent(2)	1.661(5)	1.646(8)
Fe(2)-Cent(1)	1.647(2)	1.637(2)
Fe(2)-Cent(1)	1.653(8)	1.633(7)
Fe(1)-Fe(2)	9.898(1)	9.393(3)
Fc(1) Cent(1)- Cent(2)	3.300(9)	3.291(7)
Fc(2) Cent(1)- Cent(2)	3.322(3)	3.270(1)
Cent(1)-Fe(1)-Cent(2)	177.09(1)	177.44(3)
Cent(1)-Fe(2)-Cent(2)	179.17(2)	179.20(6)
N(1)-C(13)-C(12)-C(11) ϕ	7.079(34)	8.72(23)
N(2)-C(20)-C(21)-C(22) ϕ	-1.521(3)	-10.64(24)
N(2)-C(20)-C(13)-C(12) ϕ	177.32(1)	-176.67(41)
N(1)-C(13)-C(20)-C(21) ϕ	-178.24(2)	-179.25(14)

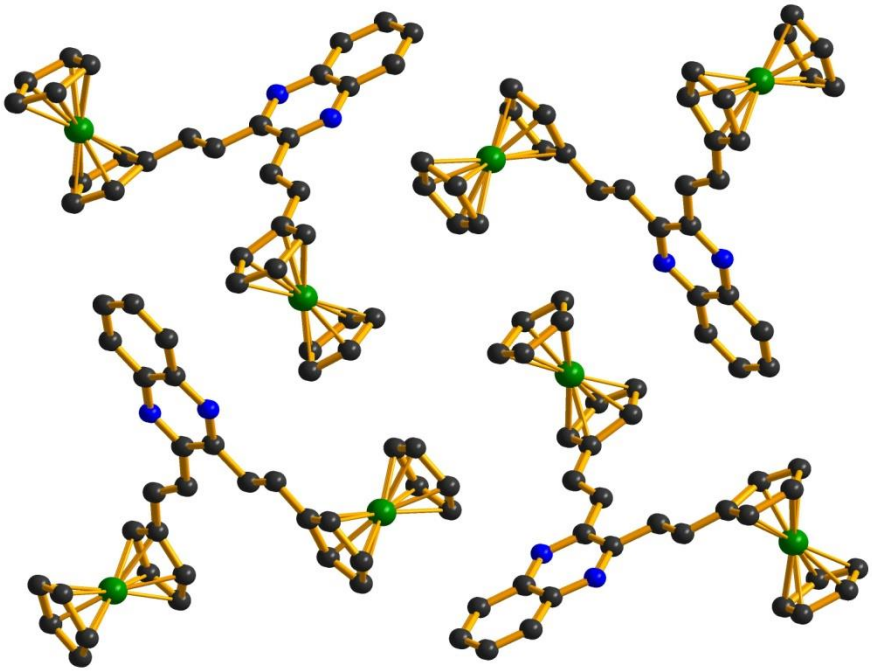


Figure S4. Crystal packing arrangement in **YQ1**.

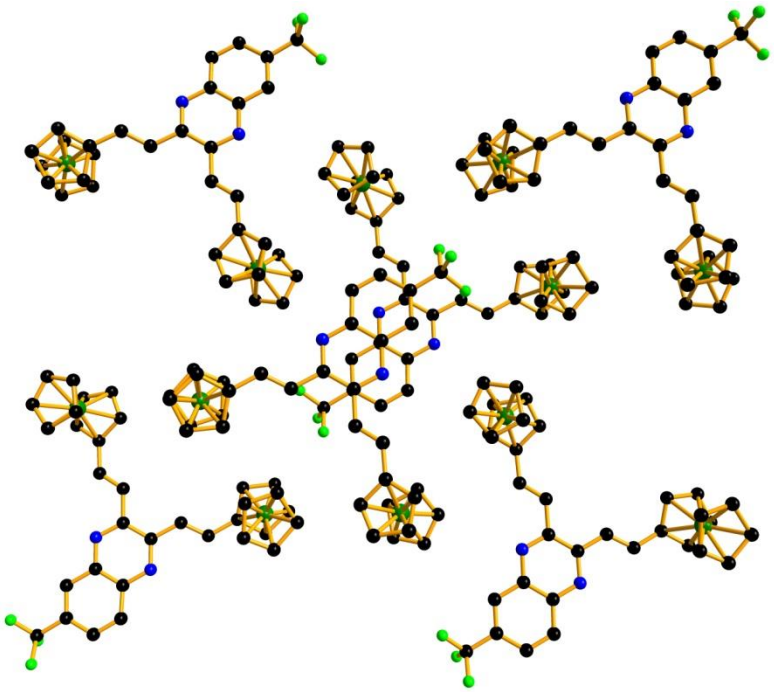


Figure S5. Crystal packing arrangement in **YQ2**.

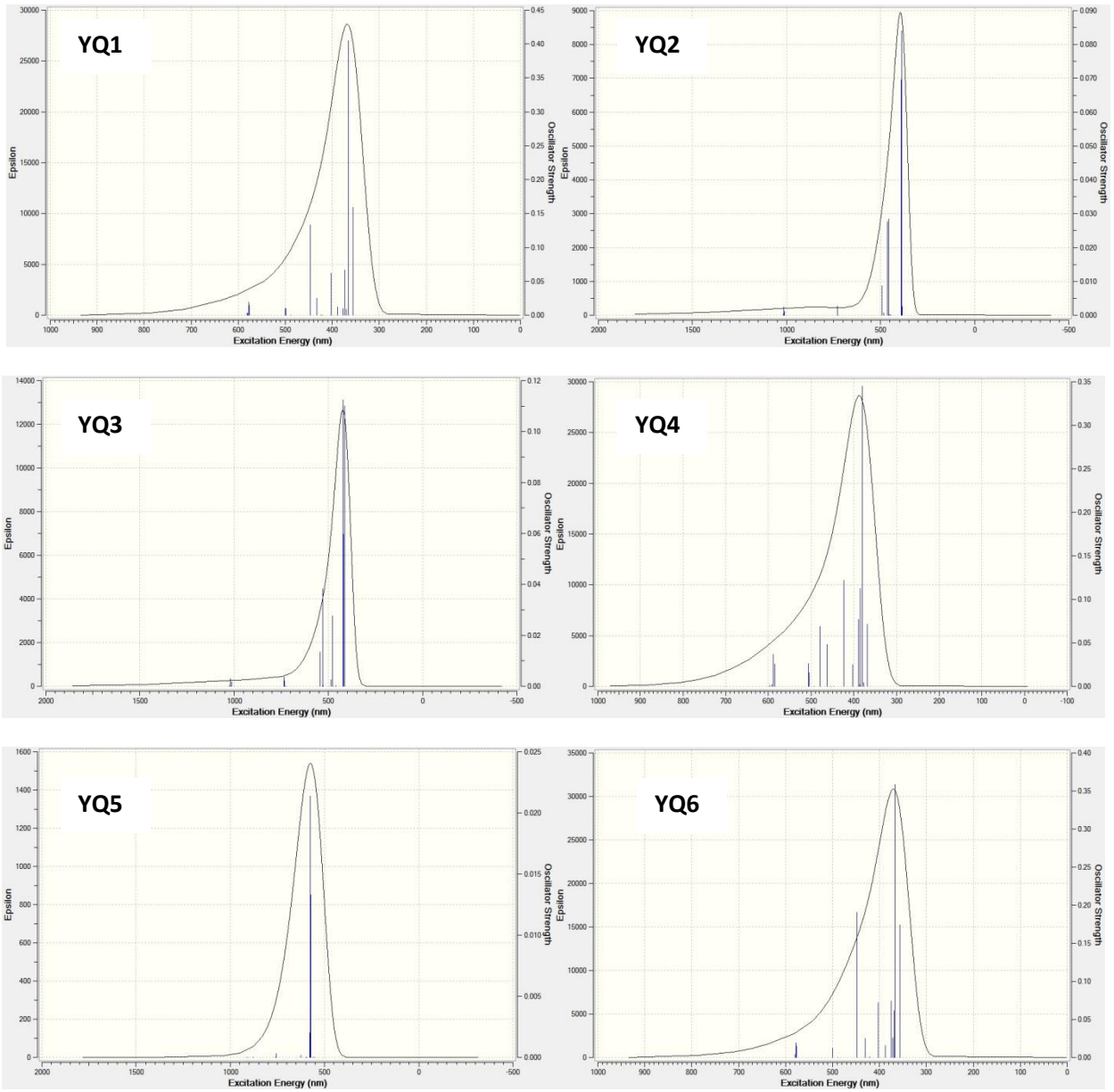


Figure S6. Theoretically calculated absorption spectra of chromophores **YQ1-YQ6**. The absorption spectra were obtained at TD-DFT/B3LYP/6-31+G** level of theory. The spectra were plotted by using GaussView 5.

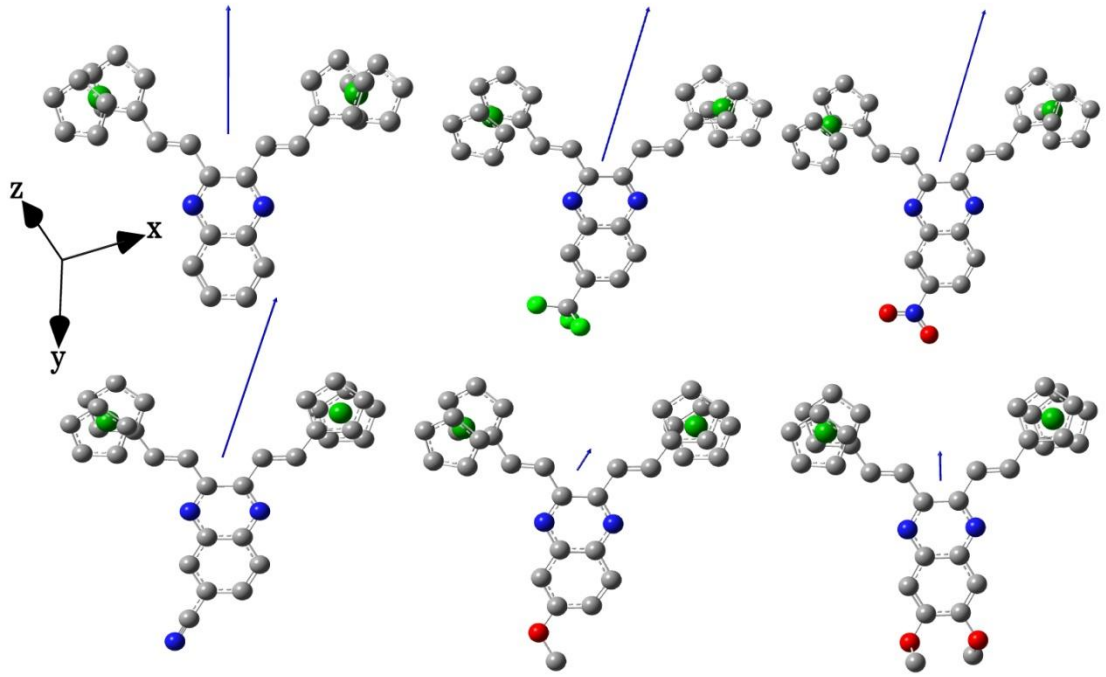


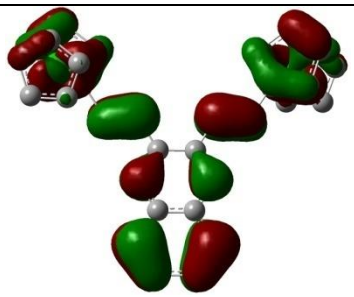
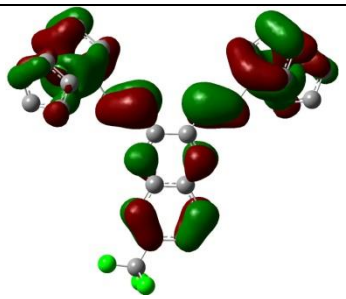
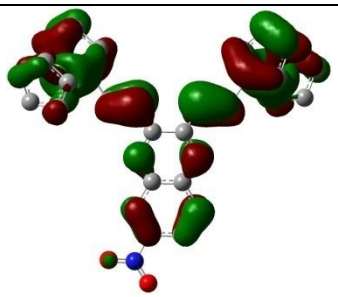
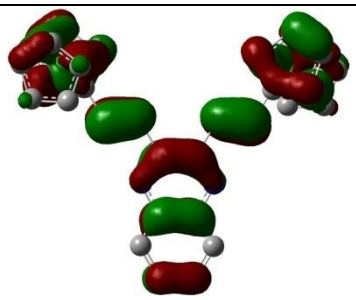
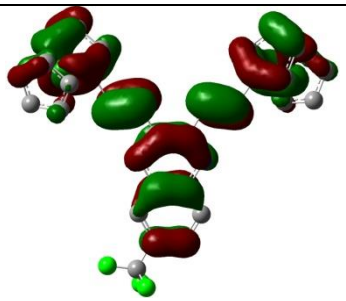
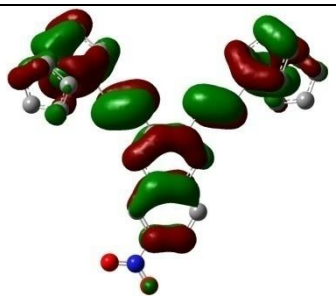
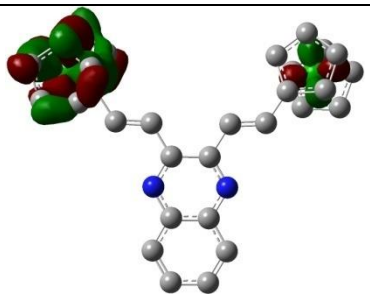
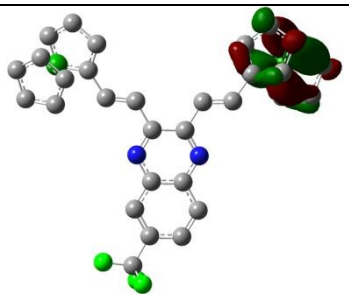
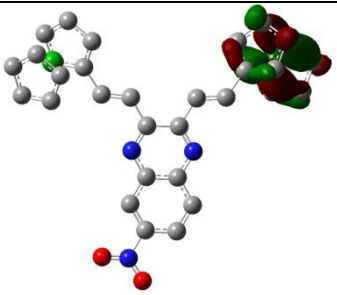
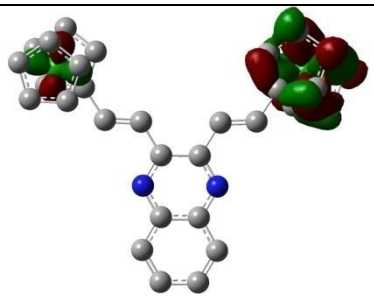
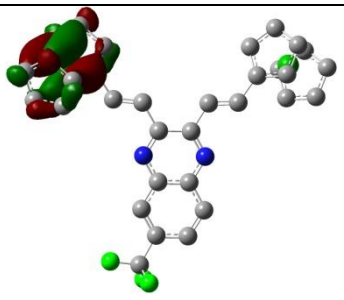
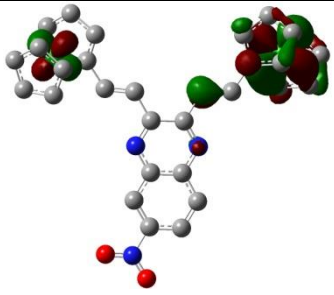
Figure S7. The energy minimized geometry of chromophores **YQ1-YQ6** and its dipole moment orientation at B3LYP/6-31+G** level of theory.

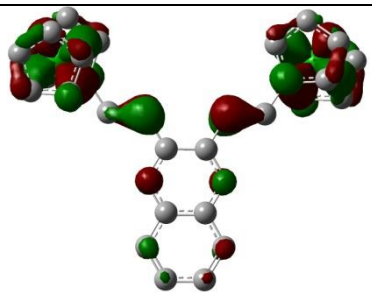
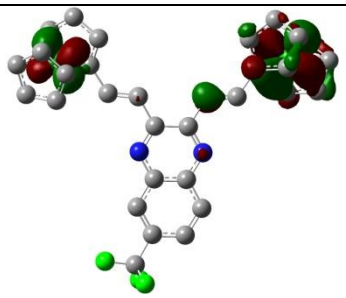
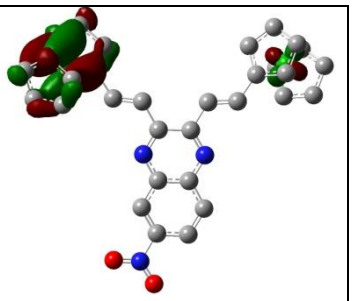
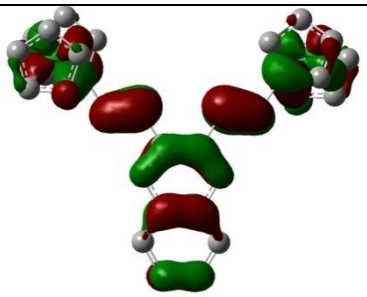
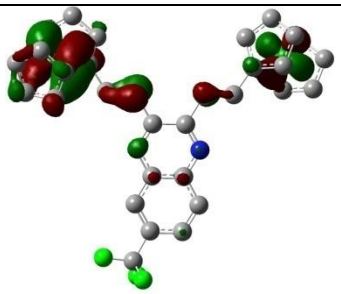
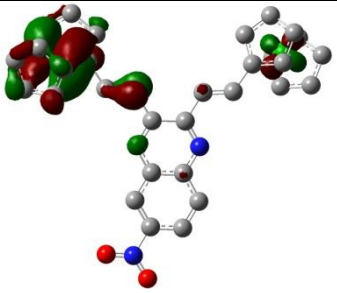
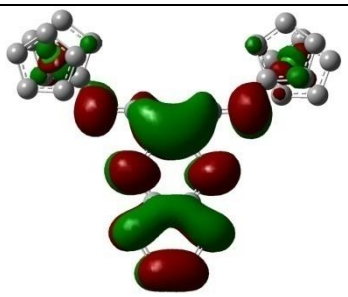
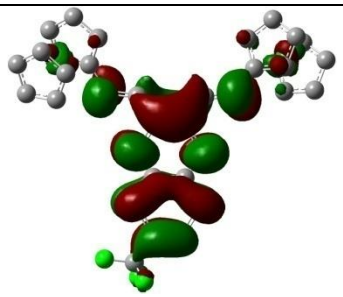
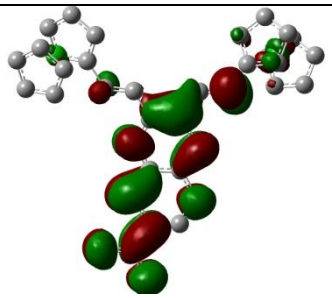
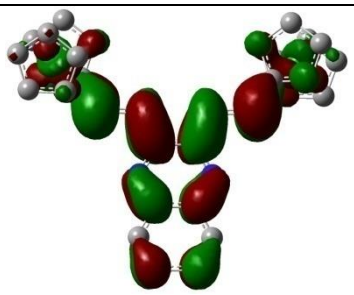
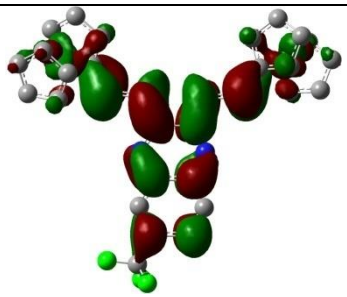
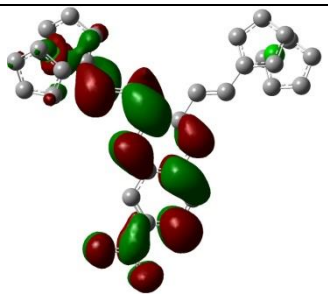
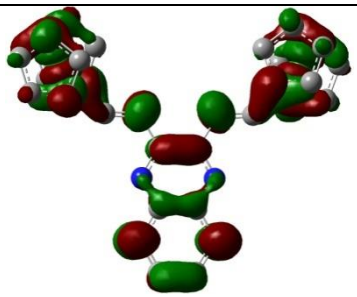
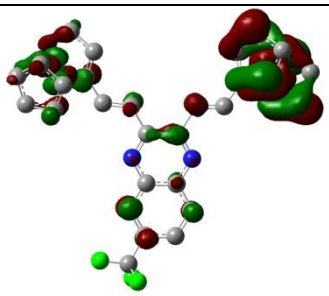
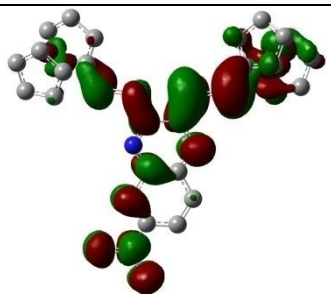
Table S3. Selected transitions obtained from TD-DFT/ B3LYP/6-31+G** level theory.

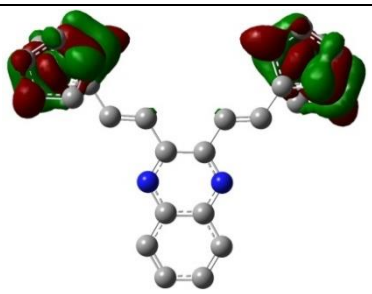
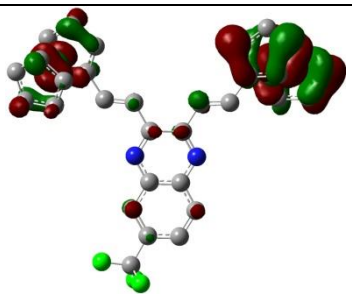
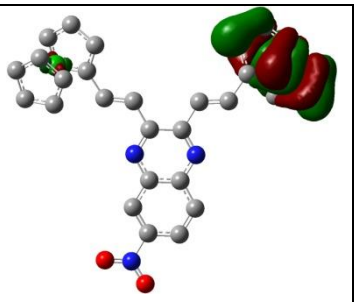
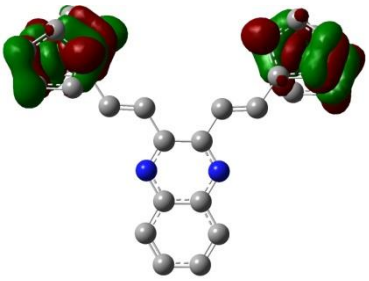
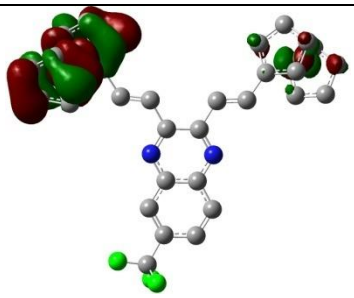
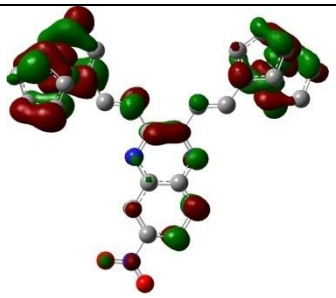
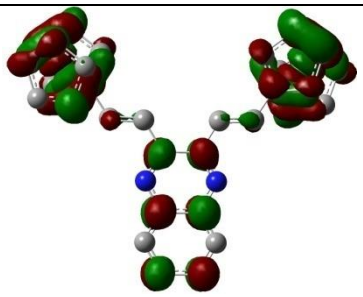
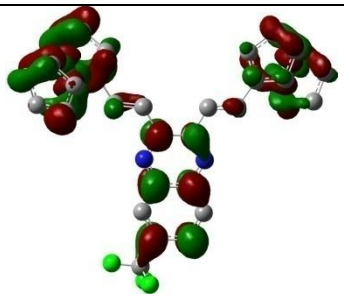
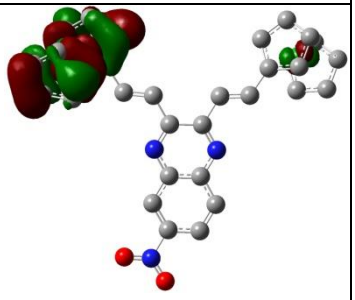
Entry	λ (nm)	Oscillator strength, *f*	Energy (eV)	[a]
YQ1	365	0.405	3.39	H-5 → L (55%)
	355	0.159	3.48	H-5 → L (31%), H-1 → L+2 (-23%)
	373	0.066	3.31	H-4 → L (41%), H-1 → L+1 (26%), H-6 → L (21%)
	402	0.061	3.08	H-4 → L (53%), H-1 → L+1 (23%)
YQ2	388	0.084	3.19	H → L+1 (43%), H-2 → L+1 (37%)
	391	0.069	3.16	H-4 → L (47%), H-1 → L+1 (30%), H → L+1 (25%)
	388	0.049	3.18	H-2 → L+1 (45%), H → L+1 (-30%), H-2 → L+5 (21%)
YQ3	422	0.112	2.93	H-4 → L (51%), H → L+1 (30%)
	414	0.110	2.98	H-2 → L+1 (49%), H-4 → L (-37%)
	420	0.059	2.94	H → L+1 (45%), H-2 → L+1 (-43%),
	421	0.012	2.94	H-1 → L+1 (53%)
	476	0.027	2.60	H-3 → L+3 (28%), H-2 → L (23%)
	529	0.038	2.33	H-2 → L (58%)
YQ4	379	0.344	3.26	H-5→ L (45%), H-7 → L (-37%), H → L+1 (30%)
	422	0.128	2.93	H-4 → L (61%)
	384	0.112	3.22	H-7 → L (58%), H-5 → L (25%), H→ L+1 (21%)
	388	0.077	3.18	H-1 → L+1 (34%), H-4 → L (28%), H-6 → L (-21)
	367	0.071	3.37	H-5 → L (32%), H-5→ L (-22%), H → L+1 (27%)
YQ5	574	0.021	2.15	H-1 → L+3 (26%), H-2 → L+5 (-25%), H-3 → L+3 (-24%)
	573	0.013	2.16	H-1 → L+7 (-30%), H-3 → L+4 (24%), H-1 → L+6 (-27%)
	578	0.002	2.14	H-3 → L+6 (30%), H-2 → L+7 (26%), H-2 → L+3 (30%)
	577	0.001	2.14	H-3 → L+7 (-30%), H-3 → L+3 (29%), H-2 → L+1 (29%)
YQ6	366	0.358	3.38	H-5 → L (50%), H → L+1 (-33%)
	356	0.174	3.48	H → L+1 (36%), H-5 → L (32%), H-1 → L+2 (22%)
	447	0.191	2.76	H → L (63%)
	374	0.074	3.31	H-4 → L (39%), H-1 → L+1 (27%), H-6 → L (-21%)
	402	0.072	3.07	H-4 → L (55%), H-1 → L+1 (20%)

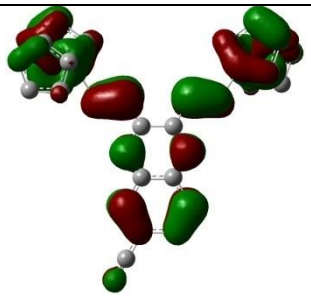
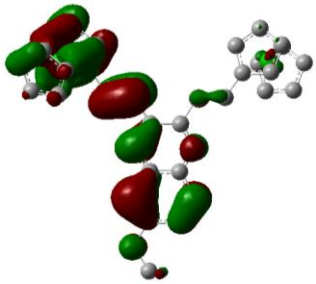
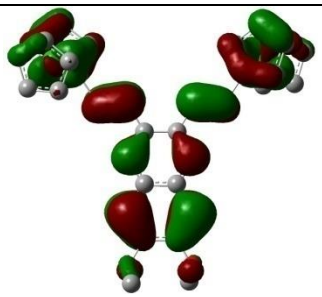
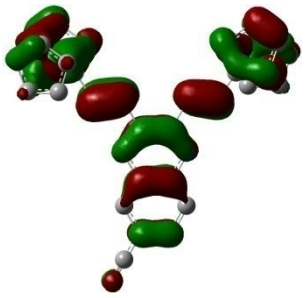
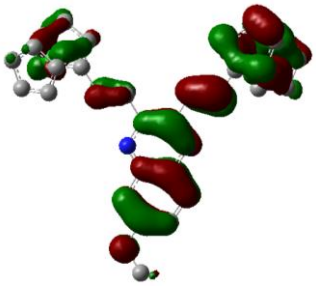
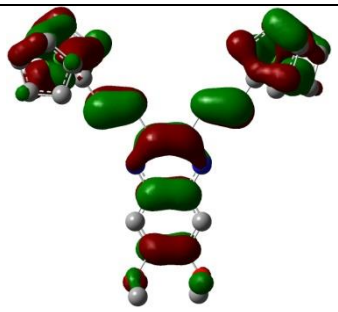
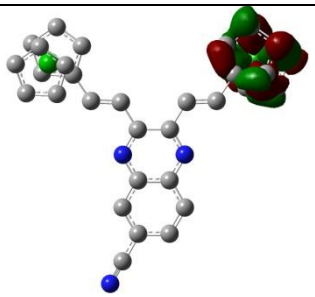
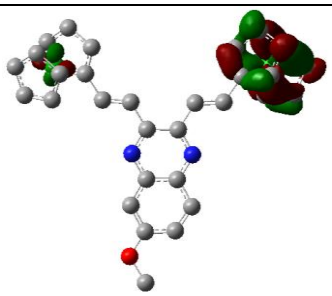
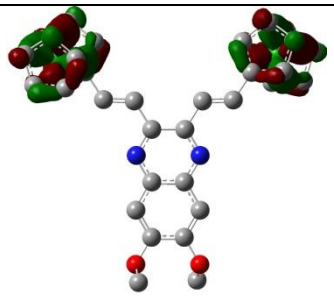
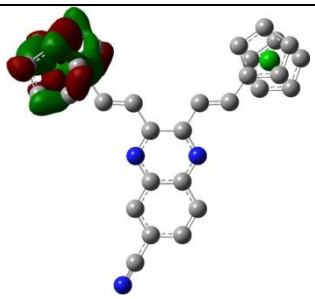
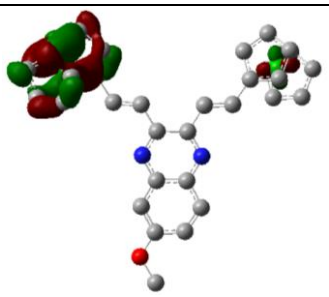
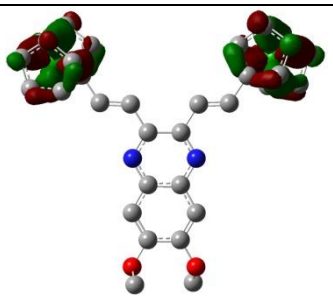
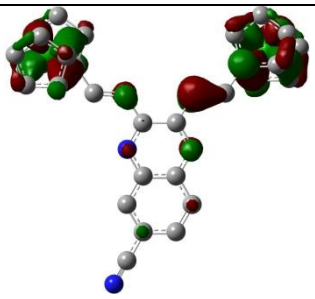
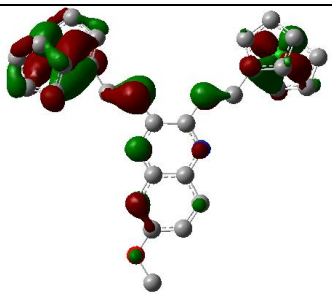
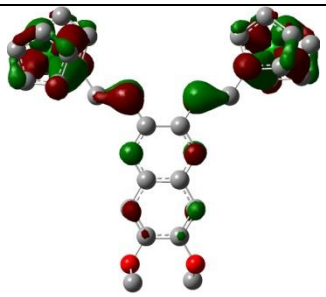
[a] H = HOMO; L = LUMO; only contributions above 10% are included.

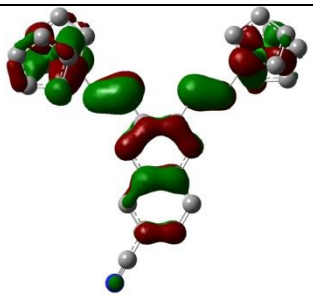
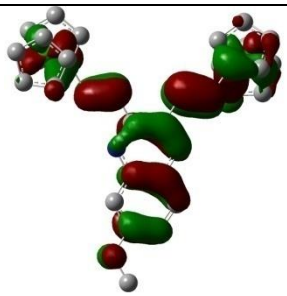
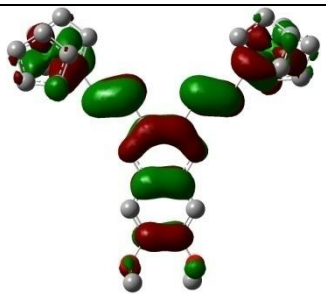
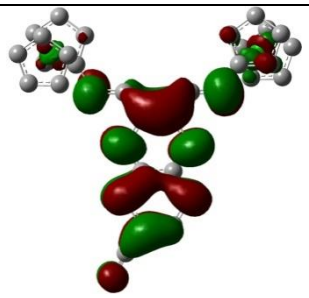
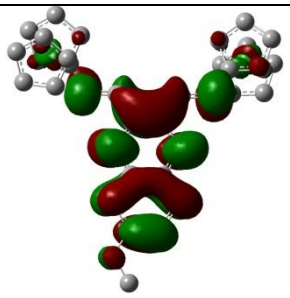
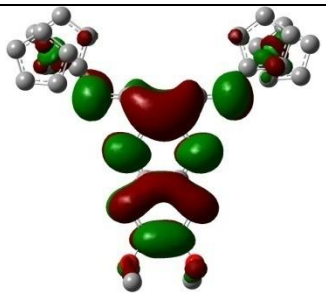
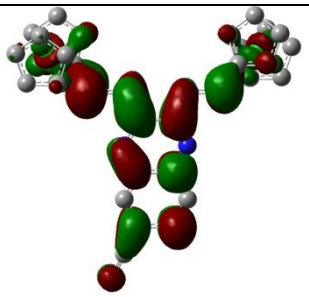
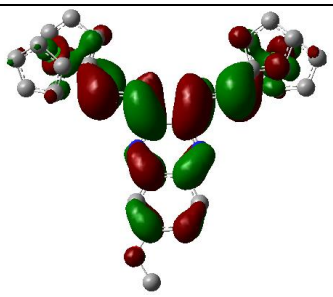
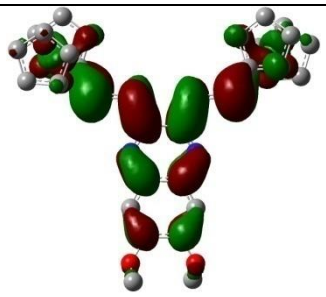
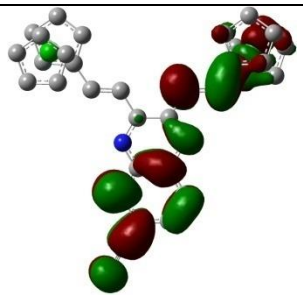
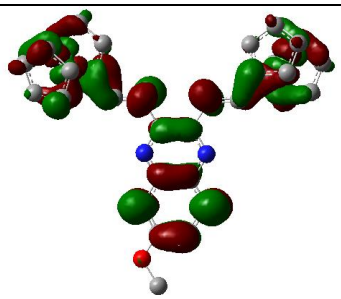
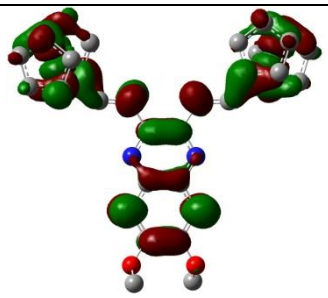
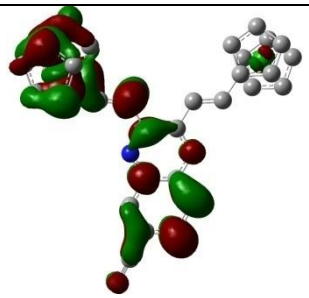
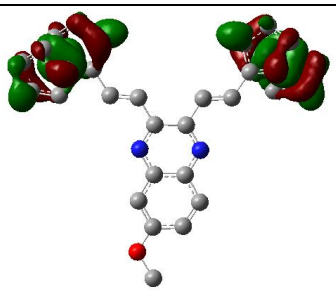
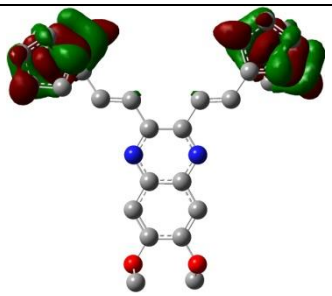
Table S4. Density surfaces of the frontier orbitals involved in electronic transitions of chromophores **YQ1-YQ6** which is derived from TD-DFT/B3LYP/6-31+G** level of theory using isosurface value of 0.02 au.

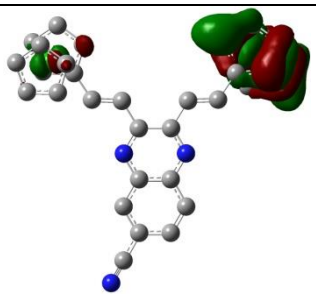
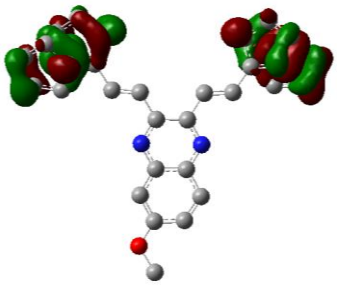
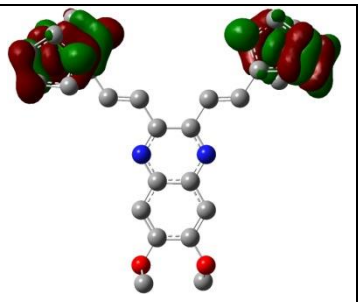
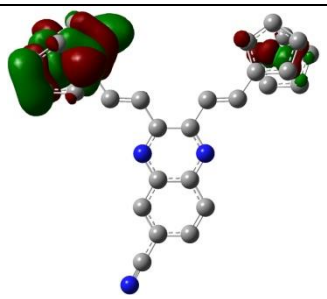
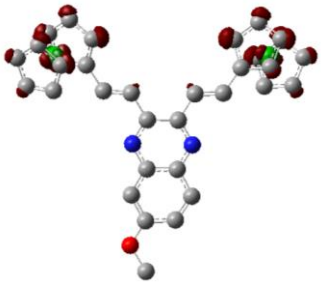
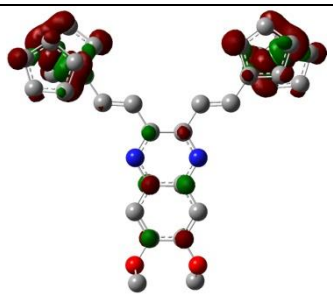
Orbitals	**YQ1**	**YQ2**	**YQ3**
HOMO-5			
HOMO-4			
HOMO-3			
HOMO-2			

HOMO-1			
HOMO			
LUMO			
LUMO+1			
LUMO+2			

LUMO+3			
LUMO+4			
LUMO+5			

Orbitals	YQ4	YQ5	YQ6
HOMO-5			
HOMO-4			
HOMO-3			
HOMO-2			
HOMO-1			

HOMO			
LUMO			
LUMO+1			
LUMO+2			
LUMO+3			

LUMO+4			
LUMO+5			

Cartesian coordinates and total energies of the optimized geometries of chromophores **YQ1-YQ6** at B3LYP/6-31+G** level of theory. Atom coordinates (in Å) and total energies (in hartrees)

YQ1

Total energy = -3871.9176055

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Fe	5.053391	-1.49306	-0.05023
2	Fe	-5.05691	-1.49018	0.051045
3	N	1.348166	2.866533	-0.40183
4	N	-1.34251	2.869317	0.401895
5	C	3.453439	-0.78986	-1.18554
6	C	4.657906	-0.85258	-1.97214
7	H	5.129487	-0.008	-2.45754
8	C	5.116197	-2.20073	-1.99627
9	H	6.005847	-2.56157	-2.49453
10	C	4.213886	-2.98601	-1.21415
11	H	4.303521	-4.04521	-1.01321
12	C	3.199285	-2.12312	-0.70693
13	H	2.386796	-2.42121	-0.05827
14	C	5.31031	-0.24559	1.587229
15	H	4.689422	0.613609	1.803626
16	C	6.487314	-0.24786	0.777581
17	H	6.918823	0.611318	0.281856
18	C	6.975559	-1.58885	0.712174
19	H	7.839966	-1.92438	0.155025
20	C	6.09862	-2.41566	1.47907
21	H	6.184205	-3.48645	1.606862
22	C	5.069107	-1.58446	2.019917
23	H	4.238866	-1.91499	2.629468
24	C	2.680885	0.421184	-0.95527
25	H	3.138897	1.354996	-1.27323
26	C	1.444458	0.476034	-0.41182
27	H	0.967259	-0.44802	-0.10842
28	C	0.701627	1.725204	-0.20548
29	C	0.687475	4.034868	-0.21008
30	C	1.355093	5.271426	-0.41524
31	H	2.39286	5.246263	-0.73281
32	C	0.685085	6.459182	-0.20967
33	H	1.196168	7.404527	-0.36657

34	C	-0.67233	6.460617	0.208662
35	H	-1.18132	7.407037	0.365846
36	C	-1.34489	5.274264	0.414012
37	H	-2.38262	5.251247	0.731873
38	C	-0.67977	4.036295	0.209163
39	C	-0.69818	1.726647	0.206254
40	C	-1.44284	0.478782	0.414458
41	H	-0.96198	-0.44738	0.123671
42	C	-2.68405	0.426747	0.947113
43	H	-3.14648	1.362212	1.253472
44	C	-3.45526	-0.78451	1.181409
45	C	-3.20106	-2.11825	0.704539
46	H	-2.39101	-2.41591	0.052584
47	C	-4.21407	-2.98117	1.215077
48	H	-4.30401	-4.04061	1.015546
49	C	-5.11523	-2.19528	1.998034
50	H	-6.00317	-2.55603	2.499458
51	C	-4.65807	-0.84682	1.970688
52	H	-5.12875	-0.00199	2.45655
53	C	-5.34591	-0.21651	-1.55999
54	H	-4.7529	0.667206	-1.75469
55	C	-5.0575	-1.53694	-2.0201
56	H	-4.213	-1.82636	-2.63102
57	C	-6.06172	-2.41342	-1.50407
58	H	-6.11076	-3.48346	-1.65501
59	C	-6.97006	-1.63337	-0.7246
60	H	-7.82635	-2.00947	-0.18101
61	C	-6.52666	-0.27555	-0.75811
62	H	-6.98992	0.557631	-0.24684

YQ2

Absolute energies = -4208.9303772

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Fe	5.727293	-1.39955	-0.05527
2	Fe	-4.80114	-2.88777	0.099824
3	N	1.230974	2.0211	-0.43902
4	N	-1.43012	1.658105	0.233455
5	C	3.804991	-1.34212	-1.13858
6	C	4.867996	-1.35745	-2.07473

7	H	5.081956	-0.58303	-2.78499
8	C	5.581354	-2.55839	-1.91892
9	H	6.441494	-2.85829	-2.48342
10	C	4.971778	-3.29319	-0.88189
11	H	5.290575	-4.2482	-0.5143
12	C	3.883715	-2.54592	-0.39707
13	H	3.237054	-2.83571	0.406874
14	C	6.005791	0.287246	1.310047
15	H	5.27244	1.05952	1.431337
16	C	7.060134	0.283804	0.375399
17	H	7.271581	1.055577	-0.33789
18	C	7.78108	-0.91677	0.534168
19	H	8.639503	-1.21656	-0.03344
20	C	7.173606	-1.65444	1.570786
21	H	7.487713	-2.61515	1.927791
22	C	6.077154	-0.91101	2.049735
23	H	5.40925	-1.20697	2.834111
24	C	2.830082	-0.25463	-1.01211
25	H	3.078669	0.661845	-1.51884
26	C	1.679994	-0.31501	-0.35065
27	H	1.392775	-1.22458	0.141422
28	C	0.758002	0.833571	-0.24232
29	C	0.405004	3.083501	-0.31243
30	C	0.899759	4.394036	-0.52468
31	H	1.931703	4.511215	-0.79827
32	C	0.075404	5.461344	-0.37815
33	H	0.443773	6.458357	-0.537
34	C	-1.28279	5.270836	-0.01127
35	C	-1.7796	4.024184	0.196173
36	H	-2.80323	3.858882	0.470354
37	C	-0.93159	2.900483	0.04646
38	C	-0.64423	0.64124	0.094871
39	C	-1.20961	-0.7123	0.270018
40	H	-0.684	-1.52812	-0.18869
41	C	-2.32681	-0.9435	0.949504
42	H	-2.81755	-0.11022	1.422209
43	C	-2.96037	-2.25208	1.139085
44	C	-2.70854	-3.46168	0.447367
45	H	-2.01468	-3.59553	-0.35833
46	C	-3.54149	-4.4595	0.984162
47	H	-3.58592	-5.48053	0.661142
48	C	-4.32143	-3.87789	2.00409
49	H	-5.05915	-4.37941	2.59797

50	C	-3.96838	-2.52058	2.097329
51	H	-4.38262	-1.8055	2.780731
52	C	-5.56909	-1.39256	-1.30086
53	H	-5.0974	-0.4412	-1.44697
54	C	-5.28466	-2.57619	-2.01225
55	H	-4.56086	-2.68072	-2.79592
56	C	-6.11116	-3.59847	-1.50608
57	H	-6.12805	-4.61758	-1.83807
58	C	-6.90723	-3.04791	-0.48091
59	H	-7.63731	-3.57389	0.101549
60	C	-6.57314	-1.68441	-0.35641
61	H	-7.00175	-0.99216	0.340865
62	C	-2.14831	6.48821	0.137524
63	F	-3.38929	6.189188	0.479061
64	F	-2.20642	7.182803	-0.99022
65	F	-1.67277	7.311232	1.061809

YQ3

Absolute energies = -4076.3791172

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Fe	5.566409	-1.4908	-0.05124
2	Fe	-5.01934	-2.37533	0.095406
3	N	1.280846	2.19278	-0.44182
4	N	-1.39739	1.968449	0.237369
5	C	3.669777	-1.29325	-1.16386
6	C	4.746456	-1.34382	-2.08342
7	H	5.0167	-0.56393	-2.768
8	C	5.386197	-2.58774	-1.95072
9	H	6.237453	-2.92134	-2.50968
10	C	4.717173	-3.31465	-0.94497
11	H	4.974207	-4.29637	-0.60019
12	C	3.665681	-2.51998	-0.45607
13	H	2.98905	-2.79471	0.328219
14	C	5.920713	0.137873	1.365214
15	H	5.234024	0.950091	1.498054
16	C	6.989507	0.09659	0.447872
17	H	7.259394	0.873536	-0.23961
18	C	7.634241	-1.14909	0.583626
19	H	8.48323	-1.48421	0.021667

20	C	6.965559	-1.8771	1.589234
21	H	7.215487	-2.86432	1.923849
22	C	5.907575	-1.08238	2.071791
23	H	5.209782	-1.35894	2.836992
24	C	2.757563	-0.15578	-1.02277
25	H	3.063105	0.755459	-1.5072
26	C	1.597454	-0.16425	-0.37454
27	H	1.252335	-1.06508	0.095102
28	C	0.743373	1.032362	-0.25454
29	C	0.515322	3.299405	-0.30215
30	C	1.083216	4.57939	-0.50452
31	H	2.118797	4.639777	-0.78125
32	C	0.326516	5.696642	-0.34603
33	H	0.733245	6.676362	-0.4927
34	C	-1.02873	5.556323	0.023513
35	C	-1.61327	4.34549	0.225687
36	H	-2.64422	4.257259	0.501673
37	C	-0.82944	3.185077	0.061238
38	C	-0.67109	0.912794	0.086005
39	C	-1.30754	-0.40962	0.249135
40	H	-0.83343	-1.24672	-0.22672
41	C	-2.42858	-0.58652	0.939163
42	H	-2.86546	0.266586	1.429105
43	C	-3.13313	-1.85885	1.11999
44	C	-2.95799	-3.07189	0.410567
45	H	-2.28234	-3.23465	-0.40521
46	C	-3.83971	-4.02739	0.945788
47	H	-3.94604	-5.04001	0.611037
48	C	-4.57345	-3.41559	1.982349
49	H	-5.3315	-3.88216	2.579043
50	C	-4.1434	-2.08187	2.08766
51	H	-4.50833	-1.35338	2.784844
52	C	-5.72277	-0.82076	-1.27348
53	H	-5.20493	0.107402	-1.41219
54	C	-5.50878	-2.00666	-2.00563
55	H	-4.80046	-2.13684	-2.79954
56	C	-6.38183	-2.99203	-1.50468
57	H	-6.45594	-4.00359	-1.85152
58	C	-7.13672	-2.41623	-0.46214
59	H	-7.88708	-2.91208	0.120945
60	C	-6.73047	-1.07419	-0.32172
61	H	-7.11473	-0.37109	0.390374
62	N	-1.83317	6.760199	0.192454

63	O	-1.29915	7.811268	0.002712
64	O	-2.97645	6.628519	0.51016

YQ4

Absolute energies = -3964.1623033

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Fe	-4.92333	-2.04191	0.064113
2	Fe	5.21307	-1.51929	-0.00508
3	N	-1.37405	2.390861	0.319027
4	N	1.289906	2.507739	-0.5688
5	C	-3.30795	-1.33656	1.167537
6	C	-4.48842	-1.43937	1.987395
7	H	-4.96046	-0.61491	2.505816
8	C	-4.91833	-2.79632	1.994881
9	H	-5.78517	-3.18645	2.511044
10	C	-4.02393	-3.54669	1.1702
11	H	-4.10082	-4.60266	0.948289
12	C	-3.04101	-2.65439	0.652917
13	H	-2.2446	-2.92098	-0.02851
14	C	-5.25685	-0.75572	-1.52987
15	H	-4.66534	0.126219	-1.73725
16	C	-6.41152	-0.81297	-0.69094
17	H	-6.85447	0.019987	-0.16169
18	C	-6.86169	-2.16808	-0.65196
19	H	-7.70316	-2.54241	-0.08453
20	C	-5.98344	-2.9485	-1.46454
21	H	-6.04491	-4.01709	-1.62134
22	C	-4.99064	-2.07477	-2.00657
23	H	-4.16787	-2.36523	-2.64607
24	C	-2.5824	-0.10166	0.922624
25	H	-3.06572	0.815246	1.252603
26	C	-1.36332	-0.00041	0.344786
27	H	-0.85814	-0.90394	0.02581
28	C	-0.68386	1.277981	0.11532
29	C	-0.76884	3.585003	0.098502
30	C	-1.48433	4.78549	0.324155
31	H	-2.50632	4.725234	0.68231
32	C	-0.87222	6.008598	0.085367
33	C	0.472391	6.067993	-0.39157

34	H	0.925501	7.036891	-0.57158
35	C	1.178808	4.908459	-0.61415
36	H	2.202995	4.930521	-0.97216
37	C	0.579059	3.643893	-0.37175
38	C	0.709086	1.339103	-0.32939
39	C	1.511221	0.12791	-0.51413
40	H	1.087789	-0.81222	-0.18229
41	C	2.750744	0.131749	-1.05763
42	H	3.148429	1.081958	-1.40692
43	C	3.609724	-1.027	-1.23125
44	C	3.453171	-2.35262	-0.69091
45	H	2.646455	-2.68803	-0.05329
46	C	4.559091	-3.14458	-1.11465
47	H	4.734672	-4.17929	-0.85239
48	C	5.419878	-2.32266	-1.90612
49	H	6.358274	-2.62723	-2.34931
50	C	4.845818	-1.02182	-1.97224
51	H	5.260282	-0.16463	-2.48643
52	C	5.313504	-0.13944	1.537902
53	H	4.629277	0.690957	1.648821
54	C	5.126931	-1.4536	2.063717
55	H	4.285902	-1.78685	2.656783
56	C	6.229552	-2.25861	1.640966
57	H	6.369034	-3.30937	1.856906
58	C	7.096968	-1.44088	0.854007
59	H	8.008002	-1.76433	0.368469
60	C	6.530138	-0.13102	0.788991
61	H	6.93904	0.712606	0.249349
62	C	-1.59009	7.22844	0.316079
63	N	-2.16091	8.22648	0.49928

YQ5

Absolute energies = -3985.7580622

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Fe	-5.02683	-2.0647	0.07026
2	Fe	5.292393	-1.59238	-0.01272
3	N	-1.37305	2.223115	0.292418
4	N	1.304657	2.359145	-0.54286
5	C	-3.27983	-1.54095	1.070925

6	C	-4.37008	-1.7215	1.993982
7	H	-4.75738	-0.95945	2.657755
8	C	-4.84603	-3.05893	1.879514
9	H	-5.66878	-3.49061	2.433464
10	C	-4.0707	-3.71768	0.875758
11	H	-4.20845	-4.73444	0.532588
12	C	-3.1148	-2.78783	0.371833
13	H	-2.40542	-2.98129	-0.42156
14	C	-5.50052	-0.53489	-1.24542
15	H	-4.92789	0.377467	-1.34549
16	C	-6.57895	-0.75345	-0.33426
17	H	-6.975	-0.03087	0.366811
18	C	-7.02074	-2.10366	-0.48855
19	H	-7.80867	-2.58364	0.076547
20	C	-6.21379	-2.71956	-1.49401
21	H	-6.2848	-3.74727	-1.82427
22	C	-5.274	-1.74929	-1.96137
23	H	-4.50871	-1.91273	-2.70822
24	C	-2.54013	-0.29989	0.896976
25	H	-2.97795	0.590398	1.343181
26	C	-1.36144	-0.1683	0.249526
27	H	-0.89143	-1.04914	-0.17316
28	C	-0.6739	1.117289	0.07442
29	C	-0.77296	3.427196	0.109218
30	C	-1.50537	4.616503	0.347296
31	H	-2.53404	4.54988	0.687351
32	C	-0.91326	5.855877	0.145318
33	C	0.420606	5.85828	-0.30438
34	C	1.187704	4.766503	-0.55259
35	H	2.21777	4.817621	-0.89364
36	C	0.587871	3.485834	-0.34148
37	C	0.721661	1.184136	-0.33641
38	C	1.535531	-0.02496	-0.50661
39	H	1.123034	-0.95878	-0.14181
40	C	2.767204	-0.02556	-1.06313
41	H	3.153666	0.917341	-1.44378
42	C	3.638782	-1.18206	-1.2075
43	C	3.520716	-2.47931	-0.59538
44	H	2.741913	-2.79101	0.087418
45	C	4.62446	-3.27855	-1.01442
46	H	4.823378	-4.29618	-0.70583
47	C	5.445906	-2.48696	-1.87546
48	H	6.372667	-2.80129	-2.33647

49	C	4.848534	-1.19897	-1.98826
50	H	5.233483	-0.36285	-2.55754
51	C	5.400746	-0.12903	1.44847
52	H	4.69887	0.689949	1.532723
53	C	5.260973	-1.41644	2.050014
54	H	4.443771	-1.73605	2.682769
55	C	6.371114	-2.21836	1.640408
56	H	6.543214	-3.25179	1.91009
57	C	7.19707	-1.42512	0.786048
58	H	8.102965	-1.75328	0.294027
59	C	6.596326	-0.13417	0.665993
60	H	6.966789	0.686564	0.066466
61	C	-0.97698	8.229074	0.160864
62	H	-1.70719	8.999863	0.409158
63	H	-0.09768	8.328111	0.807902
64	H	-0.67141	8.330574	-0.887
65	O	-1.63662	6.981167	0.382943

YQ6

Absolute energies = -4100.9657975

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Fe	-5.06323	-2.31536	0.074332
2	Fe	5.063366	-2.31564	-0.07366
3	N	-1.34906	2.049462	0.389801
4	N	1.347283	2.048756	-0.39283
5	C	-3.4537	-1.60393	1.190256
6	C	-4.6499	-1.66564	1.989224
7	H	-5.11838	-0.82024	2.47636
8	C	-5.10581	-3.01455	2.023687
9	H	-5.98943	-3.37461	2.533293
10	C	-4.20978	-3.80157	1.236006
11	H	-4.29993	-4.86175	1.040205
12	C	-3.20188	-2.93865	0.715074
13	H	-2.3969	-3.23684	0.057075
14	C	-5.38072	-1.03389	-1.52604
15	H	-4.80467	-0.13738	-1.71333
16	C	-6.55903	-1.1227	-0.72332
17	H	-7.03758	-0.30314	-0.20405
18	C	-6.97578	-2.48919	-0.7008

19	H	-7.8236	-2.88669	-0.15903
20	C	-6.05343	-3.24471	-1.48797
21	H	-6.08137	-4.31433	-1.64739
22	C	-5.06716	-2.34456	-1.99751
23	H	-4.21734	-2.61212	-2.61102
24	C	-2.68602	-0.39212	0.9464
25	H	-3.14966	0.543779	1.250151
26	C	-1.44615	-0.34063	0.41088
27	H	-0.96423	-1.26785	0.124831
28	C	-0.70109	0.90621	0.199524
29	C	-0.68623	3.214679	0.201916
30	C	-1.35747	4.451683	0.385753
31	H	-2.40192	4.452466	0.678868
32	C	-0.69344	5.641469	0.184001
33	C	0.694075	5.641056	-0.18465
34	C	1.357279	4.450974	-0.38735
35	H	2.401755	4.451189	-0.68026
36	C	0.685186	3.21429	-0.2044
37	C	0.698632	0.905868	-0.20289
38	C	1.443124	-0.34135	-0.41318
39	H	0.96019	-1.26822	-0.12771
40	C	2.684055	-0.39386	-0.94602
41	H	3.149432	0.541577	-1.24859
42	C	3.450903	-1.60656	-1.1876
43	C	3.199876	-2.93964	-0.70752
44	H	2.396845	-3.23525	-0.04598
45	C	4.20583	-3.80466	-1.22881
46	H	4.296247	-4.86419	-1.02968
47	C	5.1003	-3.02045	-2.02109
48	H	5.982502	-3.38237	-2.53185
49	C	4.64515	-1.67123	-1.98929
50	H	5.112901	-0.82735	-2.47974
51	C	5.387798	-1.02961	1.521858
52	H	4.814107	-0.13134	1.707948
53	C	5.072872	-2.33818	1.99825
54	H	4.224095	-2.60206	2.614779
55	C	6.055873	-3.24192	1.4888
56	H	6.082006	-4.31111	1.651295
57	C	6.97757	-2.49072	0.696765
58	H	7.823186	-2.89156	0.154053
59	C	6.563673	-1.12334	0.716131
60	H	7.042483	-0.30635	0.193115
61	C	1.662169	7.570063	0.802931

62	H	2.153665	8.486647	0.471794
63	H	0.753314	7.814366	1.361592
64	H	2.347806	6.99564	1.437817
65	O	1.353428	6.831284	-0.39072
66	C	-1.6592	7.573058	-0.80108
67	H	-2.1501	8.489491	-0.46866
68	H	-0.74984	7.817547	-1.35881
69	H	-2.34496	7.000284	-1.43731
70	O	-1.35183	6.831978	0.391509

References

1 R. Chauhan, M. Shahid, M. Trivedi, D. P. Amalnerkar and A. Kumar, *Eur. J. Inorg. Chem.*, 2015, 3700–3707.

2 G. Sathyaraj, D. Muthamilselvan, M. Kiruthika, T. Weyhermüller and B. U. Nair, *J. Organomet. Chem.*, 2012, **716**, 150–158.

3 (a) A. X. S. Bruker. "APEX2-Software Suite for Crystallographic Programs." Bruker AXS Inc., Madison, 2009. (b) A. X. S. Bruker. SAINT, Bruker AXS, Inc., Madison, WI, USA, 2009.

4 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112–122.

5 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786–790.

6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. a K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

7 G. M. Sheldrick, SHELXTL, Bruker AXS, Inc., Madison, Wisconsin, USA, 2008.

8 B. F. Levine, *Appl. Phys. Lett.*, 1974, **24**, 445.

9 D. Marinotto, R. Castagna, S. Righetto, C. Dragonetti, A. Colombo, C. Bertarelli, M. Garbugli and G. Lanzani, *J. Phys. Chem. C*, 2011, **115**, 20425–20432.

10 D. Marinotto, S. Proutière, C. Dragonetti, A. Colombo, P. Ferruti, D. Pedron, M. C. Ubaldi and S. Pietralunga, *J. Non. Cryst. Solids*, 2011, **357**, 2075–2080.

11 R. Macchi, E. Cariati, D. Marinotto, D. Roberto, E. Tordin, R. Ugo, R. Bozio, M. Cozzuol, D. Pedron and G. Mattei, *J. Mater. Chem.*, 2010, **20**, 1885.

12 S. Proutière, P. Ferruti, R. Ugo, A. Abbotto, R. Bozio, M. Cozzuol, C. Dragonetti, E. Emilitri, D. Locatelli, D. Marinotto, G. Pagani, D. Pedron and D. Roberto, *Mater. Sci. Eng. B*, 2008, **147**, 293–297.

13 W. N. Herman and L. M. Hayden, *J. Opt. Soc. Am. B*, 1995, **12**, 416.

14 S. Di Bella, C. Dragonetti, M. Pizzotti, D. Roberto, F. Tessore and R. Ugo, *Molecular Organometallic Materials for Optics*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, vol. 28.

15 (a) R. H. Page, M. C. Jurich, B. Beck, A. Sen, R. J. Twieg, J. D. Swalen, G. C. Bjorklund, C. G. Wilson, *J. Opt. Soc. Am. B*, 1990, **7**, 1239. (b) M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, A. Dienes, *J. Opt. Soc. Am. B*, 1989, **6**, 733.

16 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200–1211.

17 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

18 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270–283.

19 D. J. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenb, 2009.

20 GaussView, Version 5.0.9, R. Dennington, T. Keith, J. Millam, Semichem Inc., Shawnee Mission, KS, 2009.