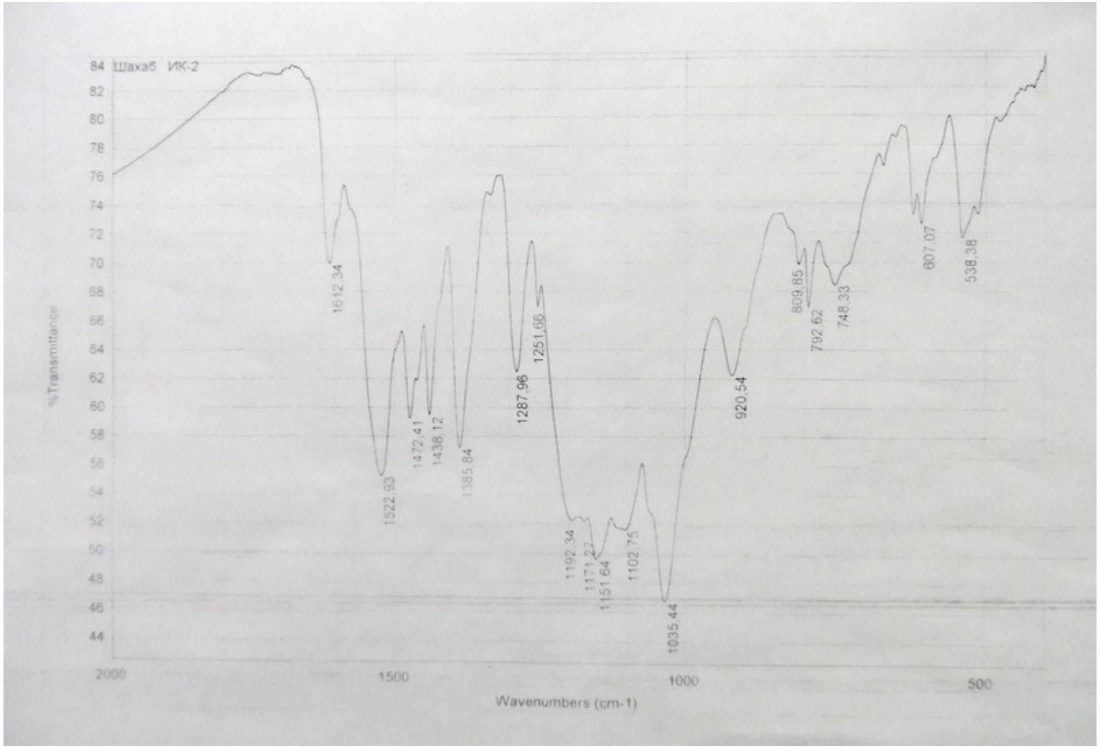
Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary data



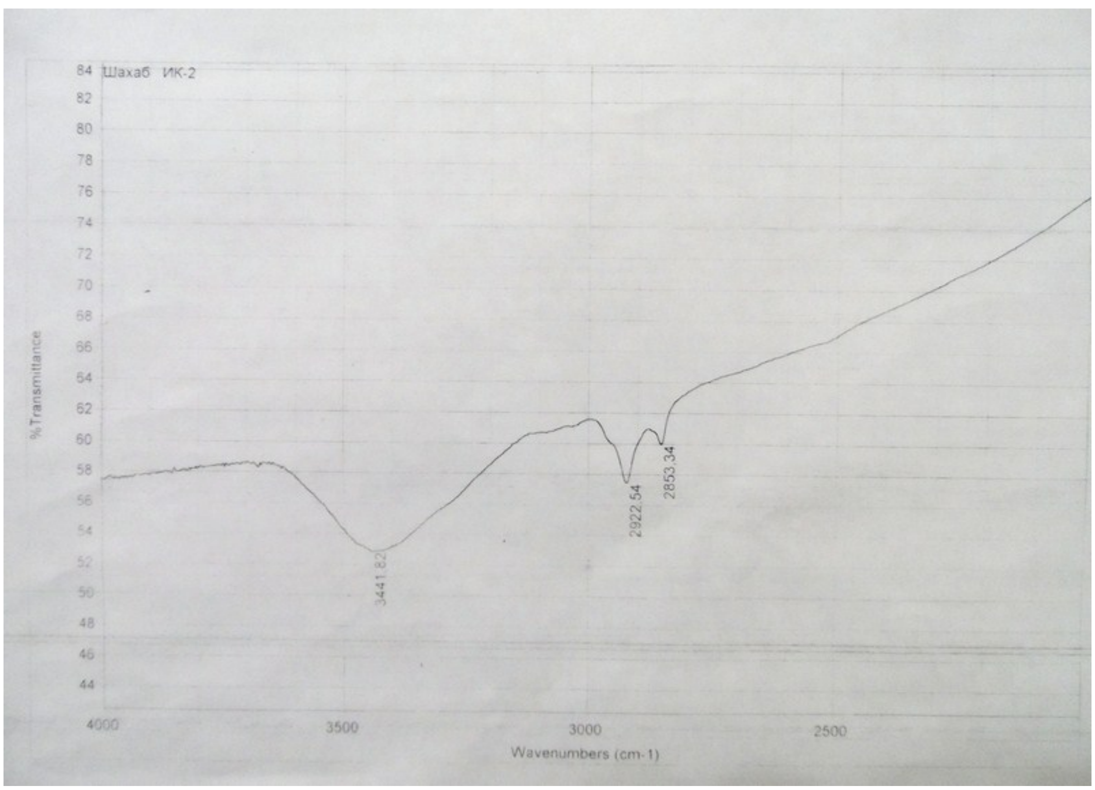


Fig. S1 Experimental FT-IR spectrum of the dye **M**

Table S2 Electronic absorption spectrum of the compound **M** calculated by TDB3LYP/6-311^{++}G* method

Excited state	Wavelength (nm)	Excitation energy (eV)	Configurations composition (corresponding transition orbitals)	Oscillator strength (f)
S_1	2869	0.43	1.02(198→199) - 0.22(199→198)	0.14
S_2	1223	1.01	- 0.10(198→200) + 0.98060(197→199)	0.02
S_3	**764**	**1.63**	**0.38(198→200) + 0.23(199→200) + 0.78(195→199) + 0.26(196→199) + 0.26(198→200)**	**2.04**
S_4	690	1.80	- 0.11(198→200) - 0.21(195→199) + 0.96(196→199)	0.00
S_5	601	2.07	0.33(198→200) + 0.30(199→200) - 0.48(195→199) + 0.73(198→200)	0.31
S_6	596	2.08	- 0.51(193→199) + 0.86(194→199)	0.00
S_7	567	2.19	- 0.26(191→199) - 0.12(192→199) + 0.81(193→199) + 0.49(194→199)	0.00
S_8	563	2.20	0.28(199→200) + 0.78(191→199) + 0.37(192→199) + 0.27(193→199) + 0.15(194→199) - 0.21(198→200)	0.06
S_9	549	2.26	- 0.20(197→200) + 0.76(199→200) - 0.22(191→199) - 0.37(192→199) + 0.15(197→200) - 0.38(198→200)	0.15
S_{10}	536	2.32	- 0.14(197→200) - 0.17(198→200) + 0.24(199→200) - 0.44(191→199) + 0.80(192→199) + 0.13(195→199) + 0.11(197→200)	0.00
S_{11}	498	2.49	- 0.34(197→200) + 0.72(198→200) - 0.31(199→200) - 0.11(188→199) - 0.13(191→199) + 0.12(192→199) + 0.10(197→199) + 0.25(197→200) - 0.33(198→200)	0.36
S_{12}	494	2.51	0.59(197→200) + 0.29(198→200) + 0.15(199→200) - 0.20(188→199) - 0.17(191→199) + 0.18(192→199) - 0.20(195→199) - 0.51(197→200) - 0.26(198→200)	0.23
S_{13}	462	2.68	- 0.16(193→200) + 0.10(197→200) + 0.23(198→200) - 0.11(183→199) + 0.12(185→199) + 0.25(187→199) + 0.78(188→199) - 0.34(189→199) - 0.14(198→200)	0.19
S_{14}	440	2.82	0.13(183→199) + 0.36(188→199) + 0.88(189→199) - 0.27(190→199)	0.00
S_{15}	432	2.87	0.28(183→199) - 0.26(185→199) - 0.25(187→199) 0.26(188→199) + 0.83(190→199)	0.00
S_{16}	426	2.91	- 0.11(199→206) + 0.49(183→199) + 0.28(184→199) - 0.39(185→199) - 0.37(187→199) + 0.15(188→199) - 0.30(189→199) - 0.48(190→199)	0.01
S_{17}	413	3.00	0.22(193→200) + 0.62(197→200) + 0.11(182→199) - 0.13(195→200) + 0.71(197→200)	0.05
S_{18}	409	3.03	0.45(183→199) - 0.35(184→199) + 0.38(185→199) + 0.69(186→199) - 0.22(187→199)	0.00
S_{19}	406	3.05	0.15(183→199) + 0.20(184→199) - 0.50(185→199) + 0.49(186→199) + 0.66(187→199)	0.00
S_{20}	405	3.06	0.61(183→199) + 0.34(185→199) - 0.48(186→199) + 0.48(187→199) - 0.14(188→199)	0.00

Table S3 Occupancy of NBOs and hybrids of the dye **M** calculated by B3LYP/6-311^{++}G* method for C, N, S, Cl atoms

Donor Lewis – type NBOs	Occupancy	Hybrid	AO (%)
σ(1) C(13) – N(14)	0.99001	$sp^{3.43}$	s(22.56%) p(77.32%)
σ(1) C(13) – N(14)	0.99001	$sp^{2.12}$	s(32.04%) p(67.94%)
σ(1) C(15) – N(14)	0.99180	$sp^{1.84}$	s(35.21%) p(64.75%)
σ(1) C(15) – N(14)	0.99180	$sp^{2.53}$	s(28.30%) p(71.61%)
σ(1) C(38) – N(14)	0.99186	$sp^{2.14}$	s(31.85%) p(68.13%)
σ(1) C(38) – N(14)	0.99186	$sp^{3.28}$	s(23.32%) p(76.56%)
σ(1) N(25) – C(24)	0.99201	$sp^{2.42}$	s(29.20%) p(70.70%)
σ(1) N(25) – C(24)	0.99201	$sp^{1.72}$	s(36.76%) p(63.19%)
σ(1) N(25) – C(26)	0.99058	$sp^{2.05}$	s(32.75%) p(67.22%)
σ(1) N(25) – C(26)	0.99058	$sp^{2.85}$	s(25.98%) p(73.92%)
σ(1) N(25) – C(34)	0.99073	$sp^{2.28}$	s(30.45%) p(69.53%)
σ(1) N(25) – C(34)	0.99073	$sp^{3.57}$	s(21.85%) p(78.02%)
σ(1) C(8) – Cl(83)	0.99410	$sp^{3.22}$	s(23.68%) p(76.15%)
σ(1) C(8) – Cl(83)	0.99410	$sp^{4.20}$	s(19.15%) p(80.34%)
σ(1) C(41) – S(88)	0.98457	$sp^{4.23}$	s(19.09%) p(80.80%)
σ(1) C(41) – S(88)	0.98457	$sp^{3.05}$	s(24.32%) p(74.18%)
σ(1) O(85) – S(84)	0.99398	$sp^{2.94}$	s(24.94%) p(73.22%)
σ(1) O(85) – S(84)	0.99398	$sp^{3.41}$	s(22.66%) p(77.22%)
σ(1) O(86) – S(84)	0.99415	$sp^{2.80}$	s(25.88%) p(72.37%)
σ(1) O(86) – S(84)	0.99415	$sp^{3.19}$	s(23.84%) p(76.03%)
σ(1) O(87) – S(84)	0.99392	$sp^{2.90}$	s(25.16%) p(73.00%)
σ(1) O(87) – S(84)	0.99392	$sp^{3.39}$	s(22.74%) p(77.14%)
σ(1) O(89) – S(88)	0.99414	$sp^{2.77}$	s(26.06%) p(72.21%)
σ(1) O(89) – S(88)	0.99414	$sp^{3.17}$	s(23.95%) p(75.92%)
σ(1) O(90) – S(88)	0.99414	$sp^{2.94}$	s(24.94%) p(73.22%)
σ(1) O(90) – S(88)	0.99414	$sp^{3.41}$	s(22.67%) p(77.20%)
σ(1) O(91) – S(88)	0.99384	$sp^{2.94}$	s(24.90%) p(73.27%)
σ(1) O(91) – S(88)	0.99384	$sp^{3.42}$	s(22.60%) p(77.27%)
LP (1) N(14)	0.88297	$p^{1.00}$	s(0.88%) p(99.12%)
LP (1) N(25)	0.80234	$p^{1.00}$	s(0.01%) p(99.98%)
LP (1) Cl(83)	0.99510	$sp^{0.24}$	s(80.79%) p(19.19%)
LP (2) Cl(83)	0.97891	$p^{1.00}$	s(0.07%) p(99.91%)
LP (3) Cl(83)	0.95551	$p^{1.00}$	s(0.02%) p(99.95%)
LP (1) O(85)	0.98215	$sp^{0.30}$	s(77.06%) p(22.94%)
LP (2) O(85)	0.92837	$p^{1.00}$	s(0.34%) p(99.60%)
LP (3) O(85)	0.92501	$p^{1.00}$	s(0.00%) p(99.94%)
LP (1) O(86)	0.99164	$sp^{0.31}$	s(76.20%) p(23.80%)
LP (2) O(86)	0.91933	$p^{1.00}$	s(0.00%) p(99.93%)
LP (3) O(86)	0.91578	$p^{1.00}$	s(0.00%) p(99.93%)
LP (1) O(87)	0.98175	$sp^{0.30}$	s(76.99%) p(23.00%)
LP (2) O(87)	0.92803	$p^{1.00}$	s(0.32%) p(99.62%)
LP (3) O(87)	0.92362	$p^{1.00}$	s(0.00%) p(99.94%)
LP (1) O(89)	0.99169	$sp^{0.31}$	s(76.08%) p(23.91%)
LP (2) O(89)	0.91839	$p^{1.00}$	s(0.01%) p(99.93%)
LP (3) O(89)	0.91556	$p^{1.00}$	s(0.00%) p(99.93%)
LP (1) O(90)	0.98190	$sp^{0.30}$	s(77.12%) p(22.88%)
LP (2) O(90)	0.93023)	$p^{1.00}$	s(0.26%) p(99.68%)
LP (3) O(90)	0.92324	$p^{1.00}$	s(0.01%) p(99.93%)
LP (1) O(91)	0.98175	$sp^{0.30}$	s(77.09%) p(22.91%)

LP (2) O(91)	0.92997	$p^{1.00}$	s(0.35%) p(99.59%)
LP (3) O(91)	0.92455	$p^{1.00}$	s(0.01%) p(99.93%)
π(2) C(13) – N(14)	0.02063	$sp^{3.43}$	s(22.56%) p(77.32%)
π(2) C(13) – N(14)	0.02063	$sp^{2.12}$	s(32.04%) p(67.94%)
π(2) C(15) – N(14)	0.01709	$sp^{1.84}$	s(35.21%) p(64.75%)
π(2) C(15) – N(14)	0.01709	$sp^{2.53}$	s(28.30%) p(71.61%)
π(2) C(38) – N(14)	0.01325	$sp^{2.14}$	s(31.85%) p(68.13%)
π(2) C(38) – N(14)	0.01325	$sp^{3.28}$	s(23.32%) p(76.56%)
π(2) N(25) – C(24)	0.01595	$sp^{2.42}$	s(29.20%) p(70.70%)
π(2) N(25) – C(24)	0.01595	$sp^{1.72}$	s(36.76%) p(63.19%)
π(2) N(25) – C(26)	0.02075	$sp^{2.05}$	s(32.75%) p(67.22%)
π(2) N(25) – C(26)	0.02075	$sp^{2.85}$	s(25.98%) p(73.92%)
π(2) N(25) – C(34)	0.01556	$sp^{2.28}$	s(30.45%) p(69.53%)
π(2) N(25) – C(34)	0.01556	$sp^{3.57}$	s(21.85%) p(78.02%)
π(2) C(8) – Cl(83)	0.01766	$sp^{3.22}$	s(23.68%) p(76.15%)
π(2) C(8) – Cl(83)	0.01766	$sp^{4.20}$	s(19.15%) p(80.34%)
π(2) C(41) – S(88)	0.09765	$sp^{4.23}$	s(19.09%) p(80.80%)
π(2) C(41) – S(88)	0.09765	$sp^{3.05}$	s(24.32%) p(74.18%)
π(2) O(85) – S(84)	0.08787	$sp^{2.94}$	s(24.94%) p(73.22%)
π(2) O(85) – S(84)	0.08787	$sp^{3.41}$	s(22.66%) p(77.22%)
π(2) O(86) – S(84)	0.08261	$sp^{2.80}$	s(25.88%) p(72.37%)
π(2) O(86) – S(84)	0.08261	$sp^{3.19}$	s(23.84%) p(76.03%)
π(2) O(87) – S(84)	0.08660	$sp^{2.90}$	s(25.16%) p(73.00%)
π(2) O(87) – S(84)	0.08660	$sp^{3.39}$	s(22.74%) p(77.14%)
π(2) O(89) – S(88)	0.08152	$sp^{2.77}$	s(26.06%) p(72.21%)
π(2) O(89) – S(88)	0.08152	$sp^{3.17}$	s(23.95%) p(75.92%)
π(2) O(90) – S(88)	0.08696	$sp^{2.94}$	s(24.94%) p(73.22%)
π(2) O(90) – S(88)	0.08696	$sp^{3.41}$	s(22.67%) p(77.20%)
π(2) O(91) – S(88)	0.08797	$sp^{2.94}$	s(24.90%) p(73.27%)
π(2) O(91) – S(88)	0.08797	$sp^{3.42}$	s(22.60%) p(77.27%)

Table S2 lists the calculated occupancies of natural orbitals. Three classes of NBOs are included, the Lewis-type orbitals, the valence non-Lewis orbital's and the Rydberg NBOs, which originate from orbitals outside the atomic valence shell. The calculated natural hybrids on atoms are also given in Table 6. As seen from Table 9, the σC(13) – N(14) bond is formed from $sp^{3.43}$ and $sp^{2.12}$ hybrids on carbon and nitrogen atoms (which is the mixture of s(22.56%) p(77.32%) and s(32.04%) p(67.94%)). This NBO corresponds to a σ(C-N) bond with approximate composition of 0.6120 C($sp^{3.43}$) + 0.7909 N($sp^{2.12}$). The weights are obtained from the squares of the coefficients as $(0.6120)^2 = 0.3745$, corresponding to 37,45% localization on carbon C(13). In a similar way the 62.54% localization on nitrogen is obtained. Overall, this describes a polar σ(C-N) bond. The σC(15) – N(14) bond is formed from $sp^{1.84}$ and $sp^{2.53}$ hybrids on carbon and nitrogen atoms (which is the mixture of s(35.21%) p(64.75%) and s(28.30%) p(71.61%)). The σC(38) – N(14) bond is formed from $sp^{2.14}$ and $sp^{3.28}$ hybrids on carbon and nitrogen atoms (which is the mixture of s(31.85%) p(68.13%) and s(23.32%) p(76.56%)). The σN(25) – C(24) bond is formed from $sp^{2.42}$ and $sp^{1.72}$ hybrids on nitrogen and carbon atoms (which is the mixture of s(29.20%) p(70.70%) and s(36.76%) p(63.19%)). The σN(25) – C(26) bond is formed from $sp^{2.05}$ and $sp^{2.85}$ hybrids on nitrogen and carbon atoms (which is the mixture of s(32.75%) p(67.22%) and s(25.98%) p(73.92%)). The σN(25) – C(34) bond is formed from $sp^{2.28}$ and $sp^{3.57}$ hybrids on nitrogen and carbon atoms (which is the mixture of s(30.45%) p(69.53%) and s(21.85%) p(78.02%)). The σC(8) – Cl(83) bond is formed from $sp^{3.22}$ and $sp^{4.20}$ hybrids on carbon and chloride atoms (which is the mixture of s(23.68%) p(76.15%) and s(19.15%) p(80.34%)). This NBO corresponds to a σ(C-Cl) bond with approximate composition of 0.6737 C($sp^{3.22}$) + 0.7390 Cl($sp^{4.20}$). The weights are obtained from the squares of the coefficients as $(0.6737)^2 = 0.4538$, corresponding to 45.38% localization on carbon C(8). In a similar way the 54.61% localization on Cl is obtained. Overall, this describes a polar σ(C- Cl) bond. The σC(41) – S(88) bond is formed from $sp^{4.23}$ and $sp^{3.05}$ hybrids on carbon and sulfur atoms (which is the mixture of s(19.09%) p(80.80%) and s(24.32%) p(74.18%)). This NBO corresponds to a σ(C-S) bond with approximate composition of 0.7138 C($sp^{4.23}$) + 0.7003 Cl($sp^{3.05}$). The weights are obtained from the squares of the coefficients as $(0.7138)^2 = 0.5095$, corresponding to 50.95% localization on carbon C(41). In a similar way the 49.05% localization on S is obtained. Overall, this describes a polar σ(C-S) bond. The σO(85) – S(84) bond is formed from $sp^{2.94}$ and $sp^{3.41}$ hybrids on sulfur and oxygen atoms (which is the mixture of s(24.94%) p(73.22%) and s(22.66%) p(77.22%)). This NBO corresponds to a σ(O-S) bond with approximate composition of 0.5876 S($sp^{2.94}$) + 0.8092 O($sp^{3.41}$). The weights are obtained from the squares of the coefficients as $(0.5876)^2 = 0.3452$, corresponding to 34.52% localization on sulfur S(84). In a similar way the 65.48% localization on O is obtained. Overall, this describes a polar σ(O-S) bond. The σ(1) O(86) – S(84) bond is formed from $sp^{2.80}$ and $sp^{3.19}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(25.88%) p(72.37%) and s(23.84%) p(76.03%)). The σO(87) – S(84) bond is formed from $sp^{2.90}$ and $sp^{3.39}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(25.16%) p(73.00%) and s(22.74%) p(77.14%)). The σO(89) – S(88) bond is formed from $sp^{2.77}$ and $sp^{3.17}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(26.06%) p(72.21%) and s(23.95%) p(75.92%)). The σO(90) – S(88) bond is formed from $sp^{2.94}$ and $sp^{3.41}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(24.94%) p(73.22%) and s(22.67%) p(77.20%)). The σO(91) – S(88) bond is formed from $sp^{2.94}$ and $sp^{3.42}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(24.90%) p(73.27%) and s(22.60%) p(77.27%)). The π C(13) – N(14) bond is formed from $sp^{3.43}$ and $sp^{2.12}$ hybrids on carbon and nitrogen atoms (which is the mixture of s(22.56%) p(77.32%) and s(32.04%) p(67.94%)). The πC(15) – N(14) bond is formed from $sp^{1.84}$ and $sp^{2.53}$ hybrids on carbon and nitrogen atoms (which is the mixture of s(35.21%) p(64.75%) and s(28.30%) p(71.61%)). The πC(38) – N(14) bond is formed from $sp^{2.14}$ and $sp^{3.28}$ hybrids on carbon and nitrogen atoms (which is the mixture of s(31.85%) p(68.13%) and s(23.32%) p(76.56%)). The πN(25) – C(24) bond is formed from $sp^{2.42}$ and $sp^{1.72}$ hybrids on nitrogen and carbon atoms (which is the mixture of s(29.20%) p(70.70%) and s(36.76%) p(63.19%)). The πN(25) – C(26) bond is formed from $sp^{2.05}$ and $sp^{2.85}$ hybrids on nitrogen and carbon atoms (which is the mixture of s(32.75%) p(67.22%) and s(25.98%) p(73.92%)). The π N(25) – C(34) bond is formed from $sp^{2.28}$ and $sp^{3.57}$ hybrids on nitrogen and carbon atoms (which is the mixture of s(30.45%) p(69.53%) and s(21.85%) p(78.02%)). The πC(8) – Cl(83) bond is formed from $sp^{3.22}$ and $sp^{4.20}$ hybrids on carbon and chloride atoms (which is the mixture of s(23.68%) p(76.15%) and s(19.15%) p(80.34%)). The πC(41) – S(88) bond is formed from $sp^{4.23}$ and $sp^{3.05}$ hybrids on carbon and sulfur atoms (which is the mixture of s(19.09%) p(80.80%) and s(24.32%) p(74.18%)). The πO(85) – S(84) bond is formed from $sp^{2.94}$ and $sp^{3.41}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(24.94%) p(73.22%) and s(22.66%) p(77.22%)). The πO(86) – S(84) bond is formed from $sp^{2.80}$ and $sp^{3.19}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(25.88%) p(72.37%) and s(23.84%) p(76.03%)). The πO(87) – S(84) bond is formed from $sp^{2.90}$ and $sp^{3.39}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(25.16%) p(73.00%) and s(22.74%) p(77.14%)). The πO(89) – S(88) bond is formed from $sp^{2.77}$ and $sp^{3.17}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(26.06%) p(72.21%) and s(23.95%) p(75.92%)). The πO(90) – S(88) bond is formed from $sp^{2.94}$ and $sp^{3.41}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(24.94%) p(73.22%) and s(22.67%) p(77.20%)). The πO(91) – S(88) bond is formed from $sp^{2.94}$ and $sp^{3.42}$ hybrids on oxygen and sulfur atoms (which is the mixture of s(24.90%) p(73.27%) and s(22.60%) p(77.27%)).