Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLYMENTARY MATERIALS

Electronic structure and large second-order non-linear optical property of COT derivatives - A theoretical exploration

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Table S1 Mean linear polarizability (α_0, au) and anisotropic polarizability ($\Delta\alpha$, au)obtained at different levels for 6-311++G(d,p)

		α_0		$\Delta\alpha$	
		CAM-B3LYP	BHHLYP	CAM-B3LYP	BHHLYP
Ia		302.3	296.5	67. 1	66.7
Ib	Scheme I	369.8	361.5	84.4	83.2
Ic		493.5	479.7	124.2	122.9
Id		543.9	528.9	96.4	92.5
IIa		1569.6	1468.5	2086.3	1892.0
IIb	Scheme II	1677.4	1569.7	2117.0	1914.1
IIc		1916.7	1793.8	2202.9	1979.9
IId		2072.3	2012.2	2005.8	1741.6
IIIa		382.4	382.3	100.3	102.5
IIIb	Scheme III	552.4	592.3	158.3	205.3
IIIc		831.7	923.2	172.1	245.4
IIId		1117.4	1231.8	458.2	524.4

Table S2. Calculated results of first hyperpolarizability (β_0, au)[a] and the ratio obtained for molecules ofdifferent **Schemes** for 6-311++G(d,p) basis set

Molecules	CAM-B3LYP	Ratio	BHHLYP	Ratio	wB97XD	Ratio
Ia	8.7 x10^2	1.0	9.0 x10^2	1.0	8.4 x10^2	1.0
Ib	4.5 x10^3	5.2	3.7 x10^3	4.1	6.7 x10^3	7.9
Ic	2.0 x 10^4	22.9	2.0 x10^4	22.2	3.4 x10^4	40.4
Id	4.1 x10^4	47.1	4. 5 x10^4	50.0	6.8 x10^4	80.9
IIa	1.6 x10^4	1.0	1.2 x 10^4	1.0	7.4 x10^4	1.0.
IIb	7.6 x10^3	0.4	4.1 x10^3	0.3	1.9 x10^4	0.26
IIc	1.4 x 10^3	0.1	1.5 x10^3	0.1	1.4 x10^4	0.2
IId	1.5 x 10^6	93.8	2.4 x 10^6	200.0	1.4 x 10^6	18.9
IIIa	5.1 x10^4	1.0	6.7 x10^4	1.0	3. 4 x10^4	1.0
IIIb	2.1 x10^5	4.1	2.9 x10^5	4.3	2.1 x10^5	6.2
IIIc	4.7 x10^5	9.2	6.0 x10^5	8.9	7.0 x10^5	20.6
IIId	1.1 x 10^6	21.6	1.1 x 10^6	16.4	1.7 x 10^6	50.0

[a]The ratio 1.0 against molecule **n**a (n = I, II and III).of each Scheme corresponds to the least β_0 value. The subsequent values: nb / na, nc / na and nd / na are multiples of β_0 of **n**a

Table S3 Transition energy (ΔE_{eg},ev), transition moment (μ_{eg}, D), and oscillator strength (f_{eg}) obtained at the TD-BHHLYP level for the 6-311++G(d,p) basis set.

Molecule	ΔE_{eg}(ev)	μ_{eg}(D)	f_{eg}
	BHHLYP	BHHLYP	BHHLYP
Ia	4.798	5.422	0.535
Ib	2.450	0.593	0.003
	3.274	1.021	0.013
Ic	1.278	1.261	0.007
	2.323	3.737	0.123
Id	1.854	2.183	0.033
IIa	1.875	6.379	0.289
IIb	1.803	6.941	0.329
	1.748	5.261	0.183
IIc	1.699	5.868	0.222
IId	1.612	5.450	0.182
IIIa	1.673	4.336	0.119
IIIb	1.096	6.768	0.190
IIIc	1.052	6.685	0.178
IIId	0.948	9.546	0.327

Table S4 Transition energy (ΔE_{eg},ev), transition moment (μ_{eg}, D), and oscillator strength (f_{eg}) obtained at the TD-wB97XD level for the 6-311++G(d,p) basis set.

Molecules	ΔE_{eg}(ev)	μ_{eg}(D)	f_{eg}
Ia	4.840	5.537	0.563
Ib	2.668	0.564	0.003
	3.291	1.076	0.015
Ic	1.308	1.081	0.006
	2.224	4.216	0.150
Id	1.909	2.112	0.032
IIa	1.727	6.067	0.241
IIb	1.664	6.788	0.291
	1.610	5.985	0.218
IIc	1.758	8.125	0.440
IId	1.573	5.456	0.178
IIIa	2.303	4.483	0.175
IIIb	1.433	5.386	0.158
IIIc	0.987	6.997	0.183
IIId	0.999	8.526	0.276

Table S5 Calculated results of first hyperpolarizability (β_0, au) obtained numerically at different levels for the 6-311++G(d,p) basis set

Molecules	CAM-B3LYP	BHHLYP	CAM-B3LYP	BHHLYP
	Numerically		Analytically	
Field strength (au)	0.001	0.001	0.001	0.001
Ia	8.8×10^2	1.0×10^3	8.7×10^2	9.0×10^2
IIa	1.7×10^4	1.2×10^4	1.6×10^4	1.2×10^4
IIIa	5.2×10^4	6.8×10^4	5.1×10^4	6.7×10^4

Table S6 Calculated results of first hyperpolarizability (β_0, au) obtained numerically at different levels for the HF/ 6-311++G(d,p) basis set

Molecule	Field Strength				
	0.008	0.009	0.001	0.0011	0.0012
Ia	1.0×10^3	1.0×10^3	1.0×10^3	1.0×10^3	1.0×10^3
IIa	2.4×10^4	2.5×10^4	2.5×10^4	2.5×10^4	2.5×10^4
IIIa	3.4×10^4	3.4×10^4	3.4×10^4	3.4×10^4	3.5×10^4

Table S7 Total number of electrons (N_e), mean transition energy (ΔE, au) and (α_0, au)[a] obtained at the CAMB3LYP level for the 6-311++G(d,p) basis set.

Molecules	ΔE	N_e	α_0
Ia	0.79	216	346
Ib	0.70	232	473
Ic	0.72	296	570
Id	0.76	360	623
IIa	0.78	256	421
IIb	0.69	272	571
IIc	0.70	336	686
IId	0.75	400	711
IIIa	0.70	204	416
IIIb	0.60	220	611
IIIc	0.64	284	693
IIId	0.70	348	710

[a] See equation 16

Table S8 Total number of electron (N_e), transition energy (ΔE_{eg}, ev) and (α_0,au)[a] obtained at the TD-CAMB3LYP level for the 6-311++G(d,p) basis set.

Molecule	ΔE_{eg}	N_e	Calculated (α_0)	$S_g \rightarrow S_e$
Ia	4.815	216	6898	$S_g \rightarrow S_{14}$
Ib	2.535	232	26731	$S_g \rightarrow S_5$
	3.217	232	16599	$S_g \rightarrow S_{13}$
Ic	1.252	296	139820	$S_g \rightarrow S_2$
	2.253	296	43177	$S_g \rightarrow S_{15}$
Id	1.844	360	78391	$S_g \rightarrow S_{12}$
IIa	1.898	256	52618	$S_g \rightarrow S_9$
IIb	1.781	272	63493	$S_g \rightarrow S_7$
	1.688	272	70682	$S_0 \rightarrow S_5$
IIc	1.652	336	91160	$S_g \rightarrow S_{12}$
IId	1.616	400	113413	$S_g \rightarrow S_{19}$
IIIa	1.833	204	44956	$S_g \rightarrow S_3$
IIIb	1.232	220	107321	$S_g \rightarrow S_3$
IIIc	0.957	284	229604	$S_g \rightarrow S_2$
IIId	0.983	348	266660	$S_g \rightarrow S_4$

[a] See equation 18

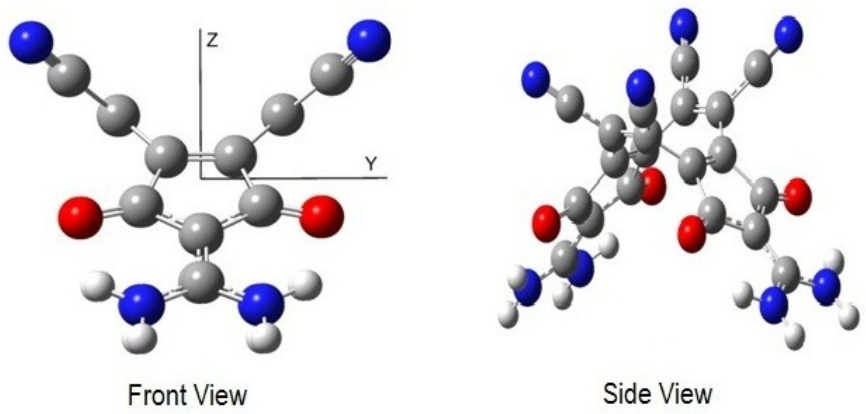


Fig.S1a COT derivate Ia (**Scheme I)**

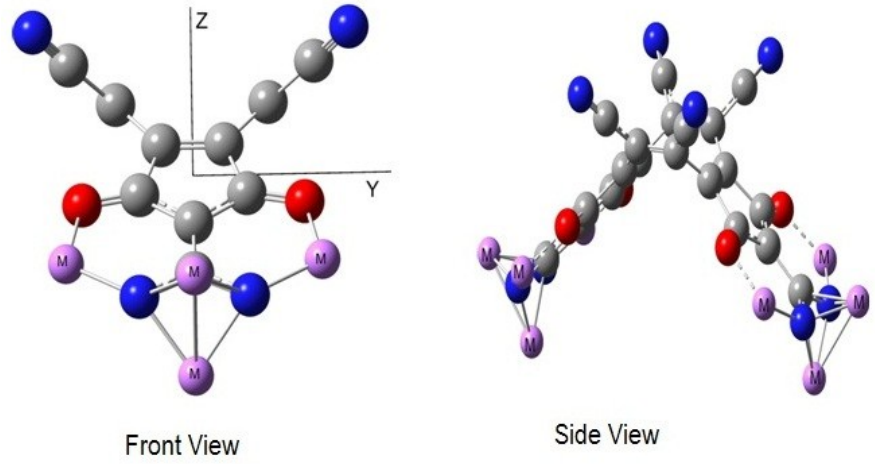


Fig.S1b COT derivates of metal–amine complexes (**Scheme I)**

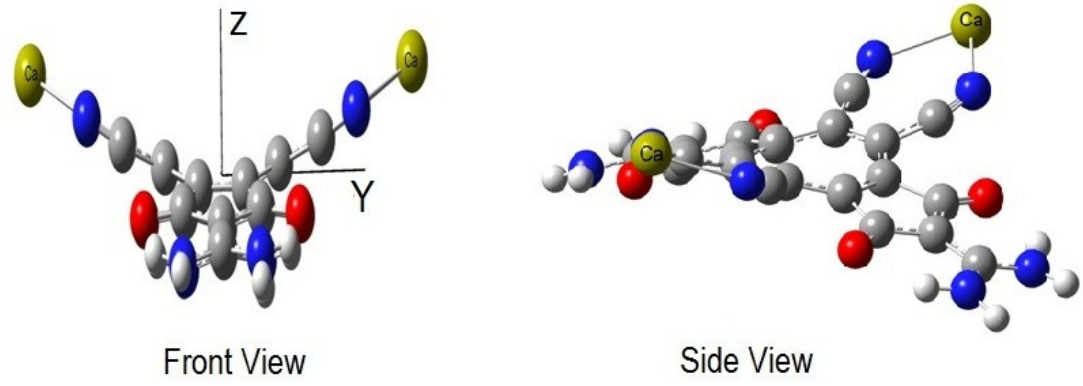


Fig.S2a COT derivate IIa (**Scheme II**

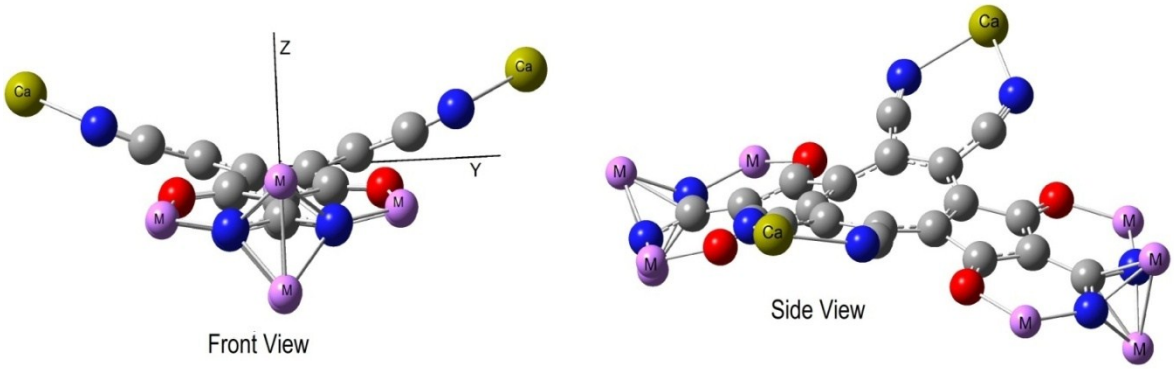


Fig.S2b COT derivates of metal –amine complexes (**Scheme II)**

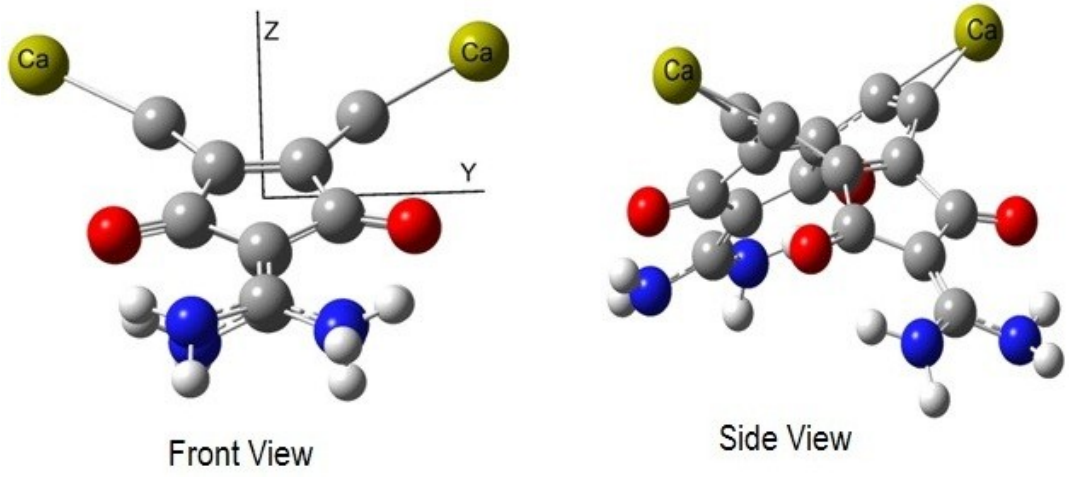


Fig.S3a COT derivate **IIIa** (**Scheme III)**

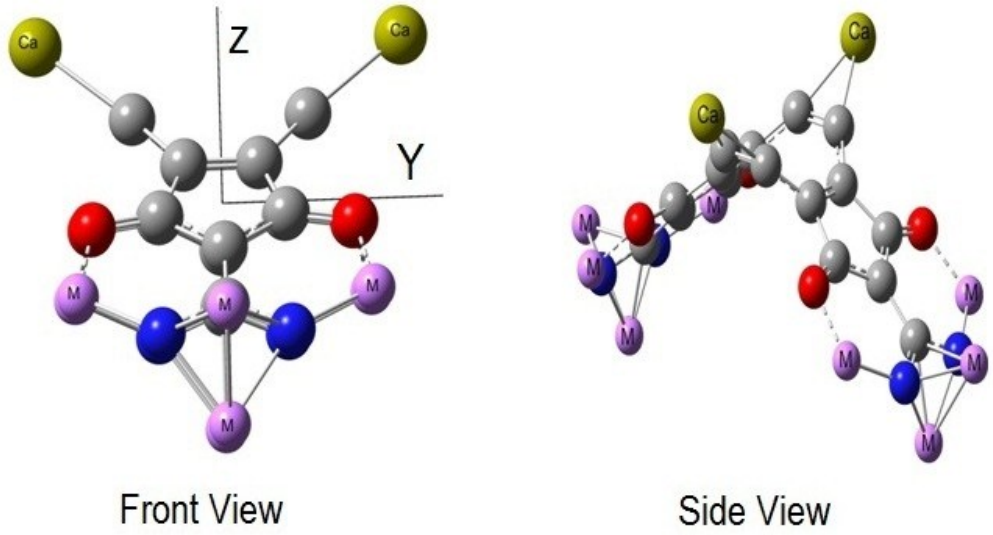


Fig.S3b COT derivates of metal –amine complexes (**Scheme III)**

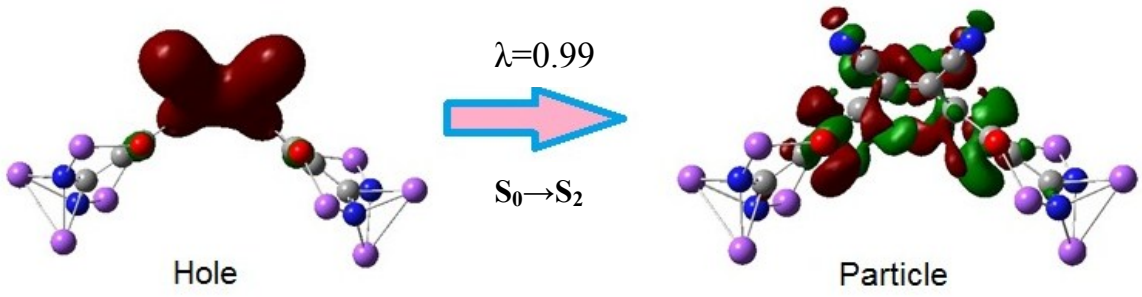


Fig.S4a NTO picture for 1c

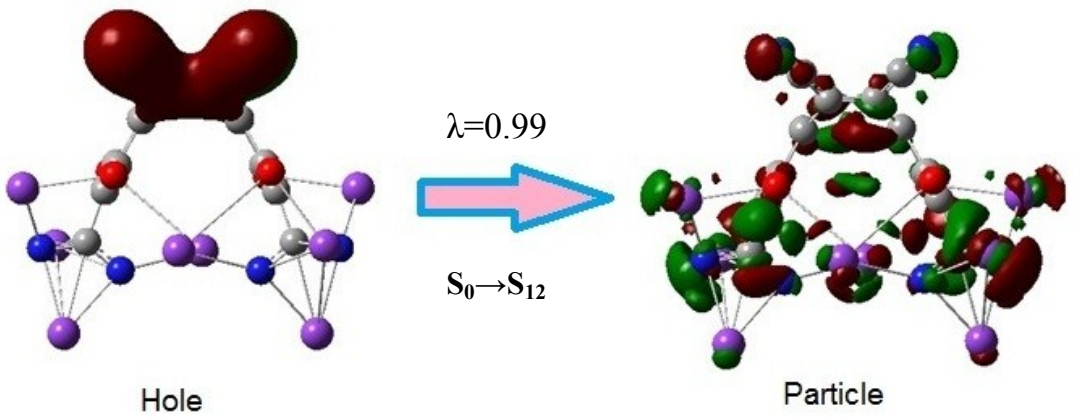


Fig.S4b NTO picture for 1d

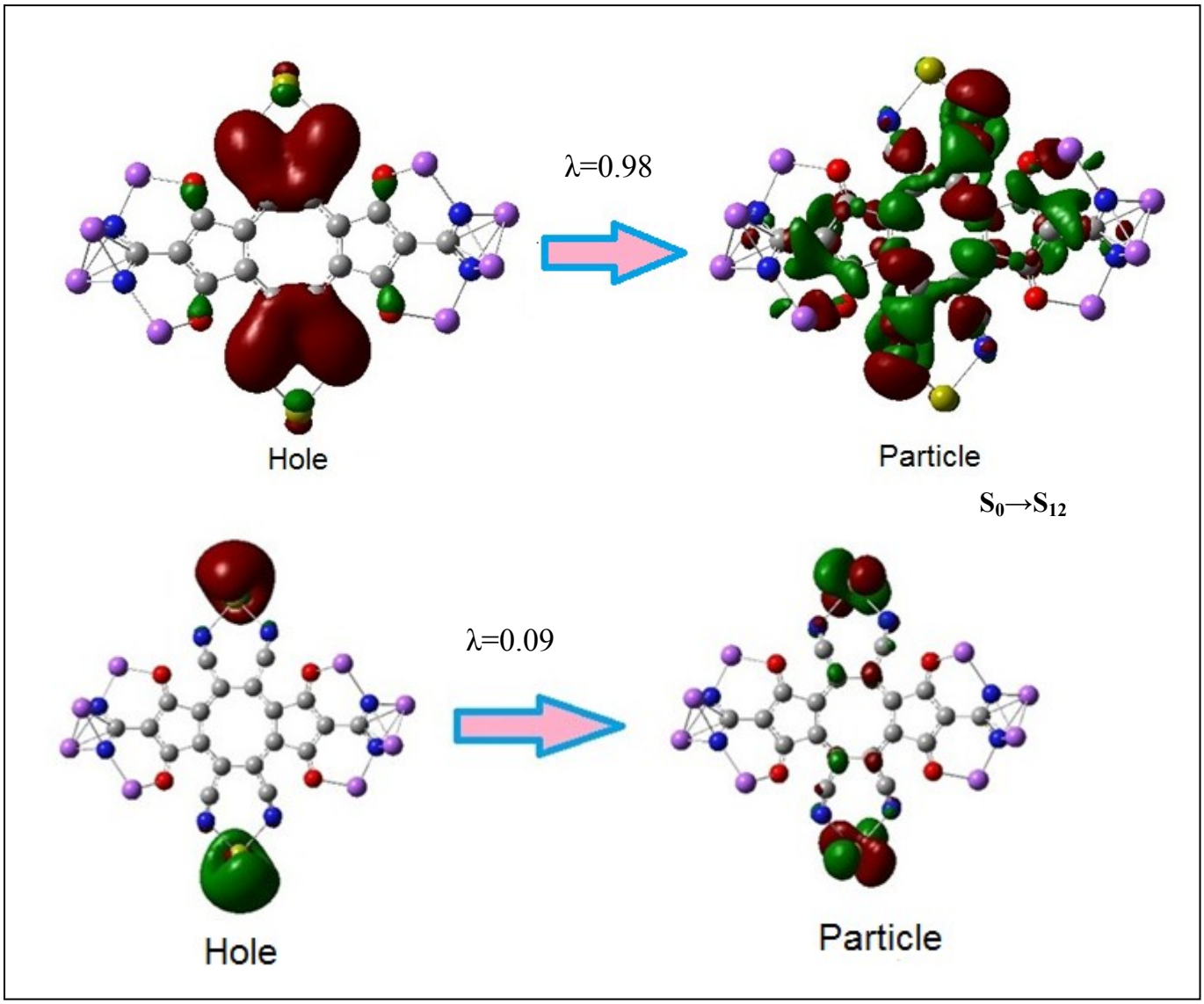


Fig.S5a NTO picture of **IIc**

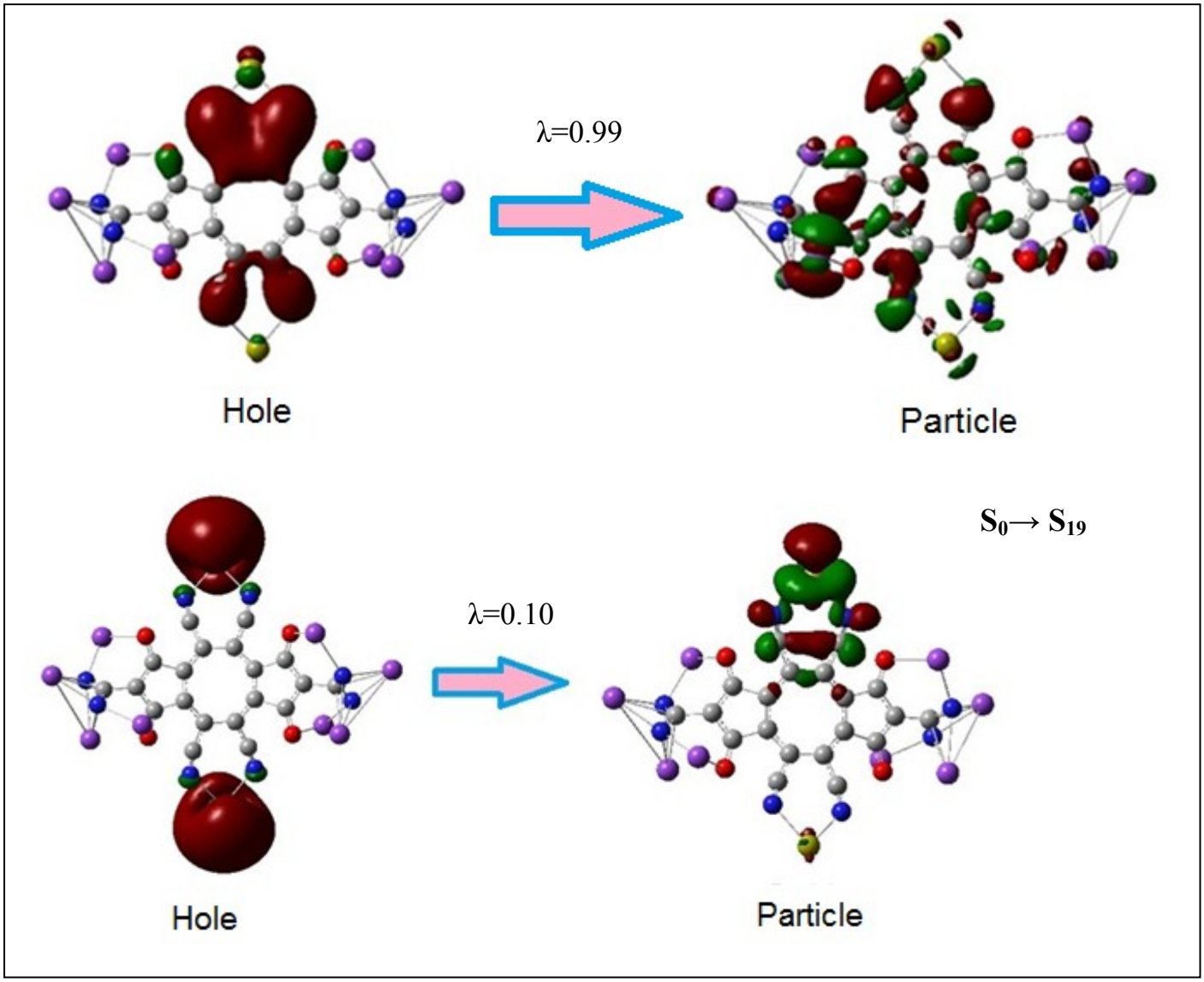


Fig.S5b NTO picture of **IId**

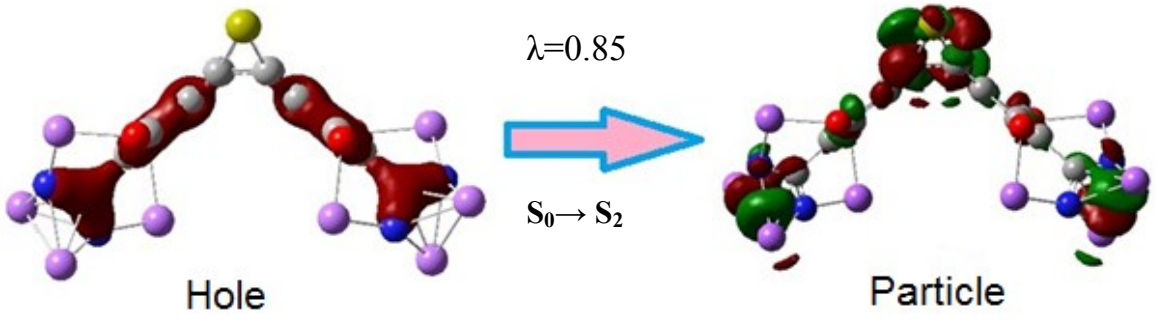


Fig.S6a NTO picture for IIIc

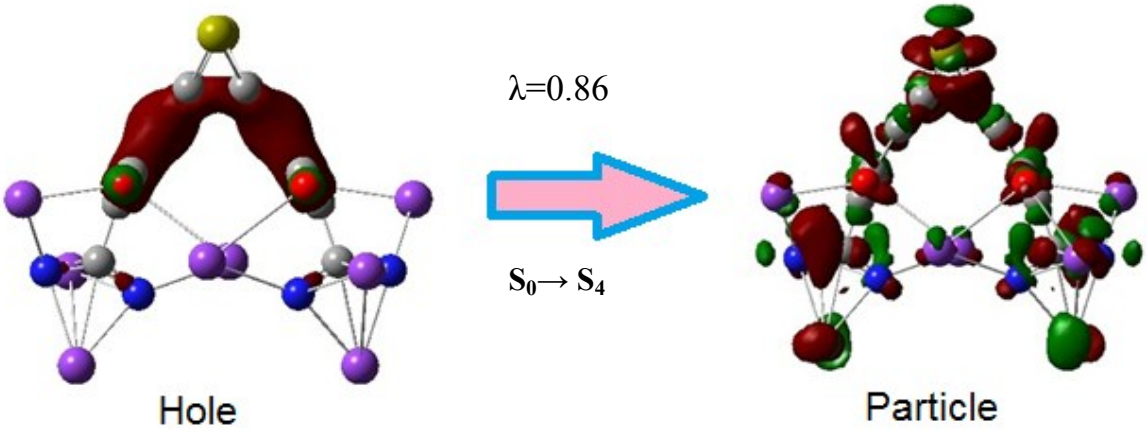
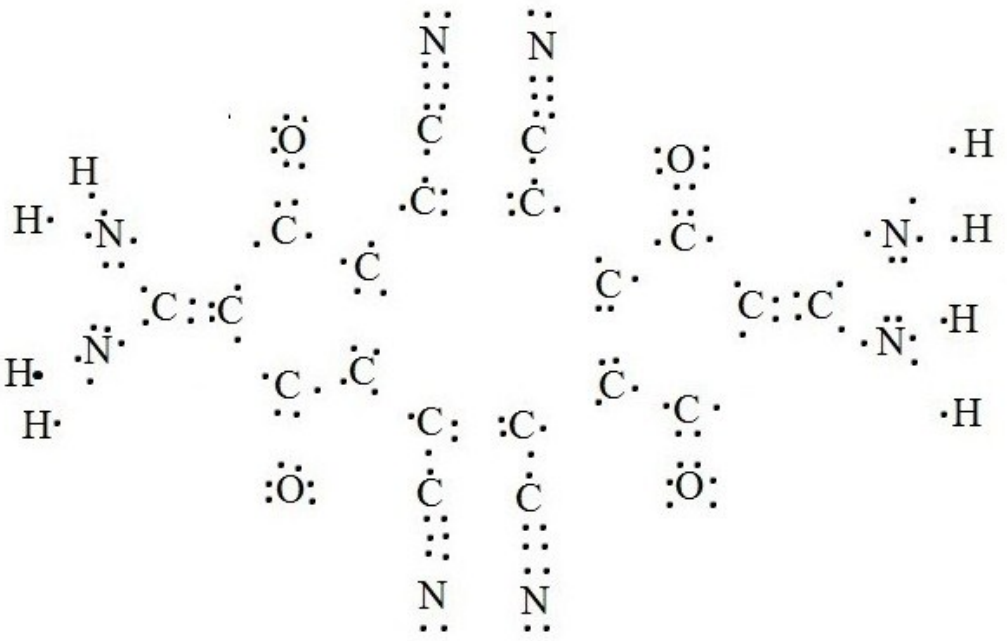
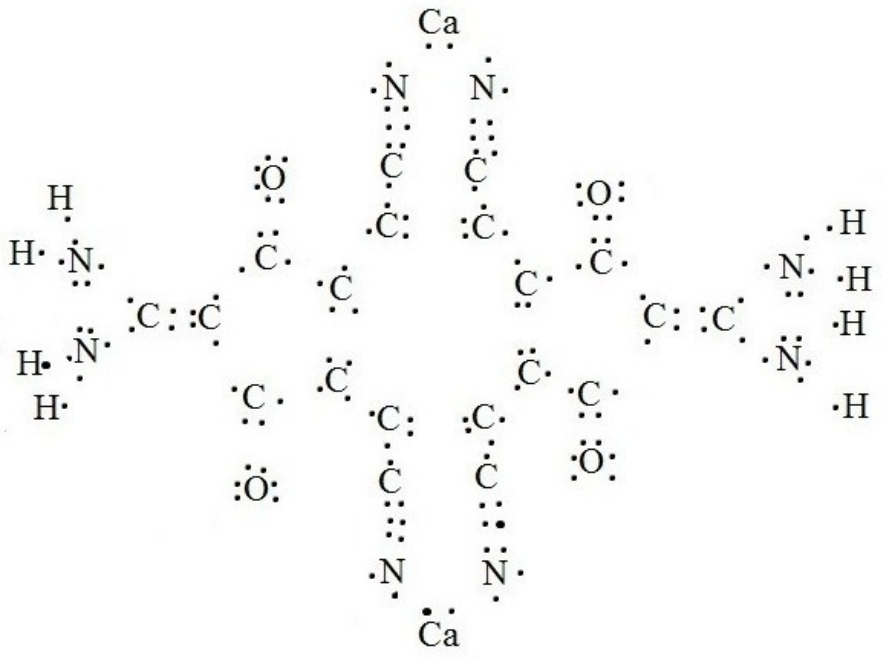


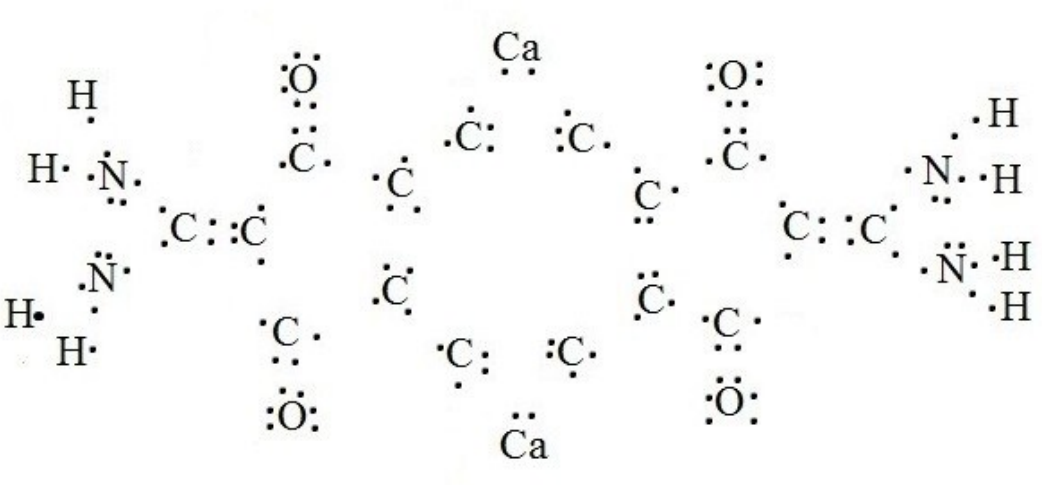
Fig.S6b NTO picture for IIId



Ia



IIa



IIIa

Fig.S7 Lewis structure of the representative molecule of each Scheme **na**.