Light-induced reversible switching of generation and extinction of an organic radical anion

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Materials and instrument:

All the reagents employed were commercially available from commercial sources and were used without further purification. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA), 4-aminophenylboronuc acid hydrochloride, triethylamine was purchased from Sigma-Aldrich. $CDCl_3$(Cambridge Isotope Laboratories, 99% D) was used in NMR. Solvents were purified and dried by standard methods. Tetrahydrofuran (THF) was distilled freshly over sodium/benzophenone and anhydrous CaH_2, respectively, prior to use. All other solvents used for synthesis and purification were freshly distilled prior to use. A dry nitrogen/argon atmosphere was maintained during the reactions using flame-dried glassware, unless otherwise indicated. Column chromatography was carried out with a silica-gel of 100-200 mesh, Merck. Reactions were monitored by thin-layer chromatography (TLC) using Merck plates (TLC Silica Gel 60 F254). Yields refer to use of chromatographically and spectroscopically pure compounds. The structures of the compounds were determined by NMR spectroscopy, mass spectrometry, and a plethora of other spectroscopic techniques. ^{1}H NMR spectra were recorded on 400 MHz Jeol and 500 MHz Bruker spectrometer. Chemical shifts are reported as δ values relative to an internal reference of tetramethylsilane (TMS) for ^{1}H NMR or the solvent peak. In the case of ^{13}C NMR the solvent peak was used for calibration. ^{13}C NMR spectra were recorded on 125 MHz Bruker spectrometers with complete proton decoupling. High-resolution mass spectra (HRMS) data were obtained from an Acquity ultraperformance Bruker MaXis Impact liquid chromatography instrument using a positive mode electrospray ionization (Q-TOF) instrument. The spectroscopic grade solvents for the spectroscopic experiments were distilled and checked prior to their use to ensure that they were free from any fluorescent impurity. The absorption spectra were monitored in Agilent cary-60 UV spectrophotometer and emission were measured in Horiba Duetta fluoremeter using 1cm path length cuvette (Starna). The low temperature UV-vis experiment was performed in Agilent diode array Cary-8454 spectrophotometer attached with Unisoku cryostat. X-band electron paramagnetic resonance (EPR) spectra were recorded using an EMX MICRO X Bruker EPR instrument.

Computational details:

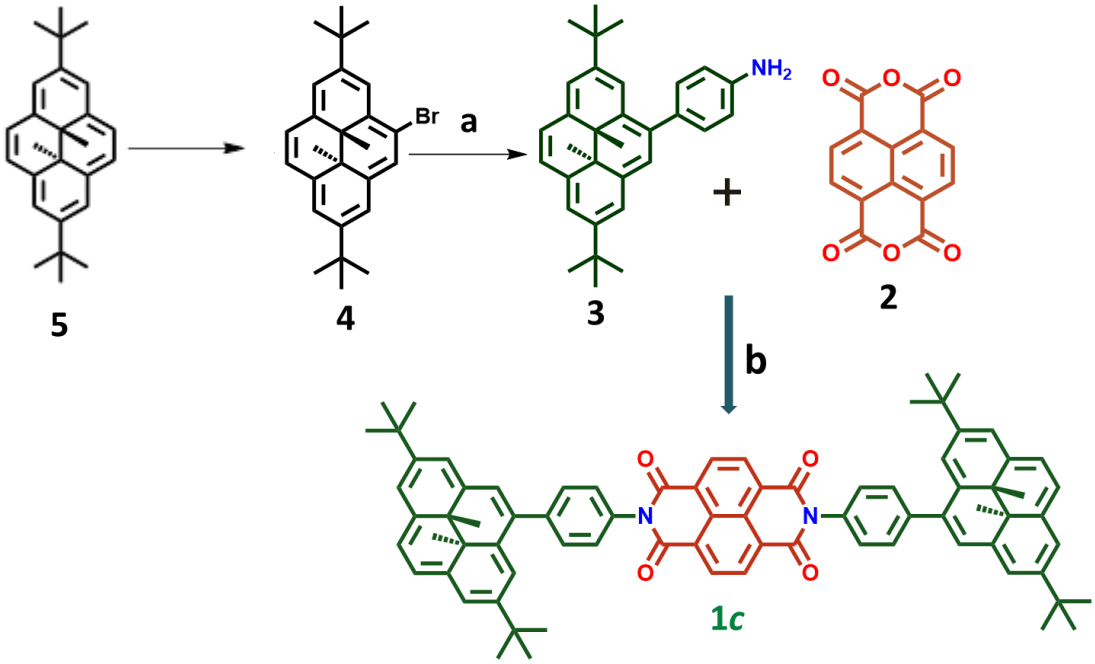
The Gaussian 16 program (Revision A.03) was used for all the calculations unless specified.[1] Geometry optimizations were performed using the CAM-B3LYP functional in combination with 6-311G(d) basis set on all atoms. All calculations employed a polarizable continuum model (PCM) for DMF for all atoms.[2] Frequency calculations performed on the optimized geometry using same functional/basis set combination confirmed the optimized geometries were located at a minimum on the potential energy surface. Single point and TD-DFT calculations[3,4] using the optimized geometry were performed in the same CAM-B3LYP/6-31g(d) level considering the solvent effect (PCM model, DMF as solvent).

Experimental section:

Light sources used in photochemical processes:

Both the 525 nm and 370 nm light sources used in this project were bought from Kessil[5] having an average intensity of 399mW/cm^2 (measured from 1 cm distance). Power consumption of 40 W for both 370 nm and 525 nm light sources.

Synthesis and characterization:



a) 4-aminophenylboronic acid hydrochloride (2.3 eq), $Pd(PPh_3)_4$ (8 mol%), K_2CO_3 (2.4 M), dry THF (3 mL), 85 ^oC, 20h, N_2 (yield 70%); b) 1,4,5,8-naphthalenenetetracarboxylic dianhydride (1 eq), **3** **(**2.2 eq), Et_3N, dry DMF, 140 ^0C, 16h, N_2 (yield 40%).

The unsubstituted DHP was synthesized according to the reported literature.[6] The purity of the synthesized compound was confirmed from ^1H NMR data which was consistent with the reported values. Bromination of the parent DHP was done following the reported procedure to afford the bromo-DHP **3** and the ^1H NMR data was consistent with the literature.[7]

4-((3a^{1}R,5a^{1}R)-2,7-di-tert-butyl-3a^1,5a^1-dimethyl-3a^1,5a^1-dihydropyren-4-yl)aniline (3): 200 mg (0.47 mmol, 1 eq) of **4** was dissolved in THF (3 mL) and to it, 187 mg (1.08 mmol, 2.3 eq) of 4-aminophenylboronic acid hydrochloride, 583 mg (4.2 mmol, 9 eq) of K_2CO_3 and 10 mol% of $Pd(PPh_3)_4$ were added. The mixture was purged with N_2 and kept in stirred for 16 h at 80 ^oC under N_2 atmosphere. The resulting mixture was washed with ethyl acetate. The organic layer was separated and dried over anhydrous Na_2SO_4. The desired product (dark green, 130 mg, yield 65%) was purified through column chromatography over silica gel using dichloromethane as an eluent. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.69 (s, 1H), 8.50 (s, 3H), 8.46 (s, 1H), 8.41 (s, 2H), 7.65 (d, J = 8.4 Hz 2H), 6.94 (d, J = 8.4 Hz 2H), 3.83 (bs, 2H) 1.69 (s, 9H), 1.61 (s, 9H), –3.83 (s, 6H), –3.85 (s, 3H). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$) δ 145.6, 145.1, 136.8, 136.6, 136.4, 135.1, 133.3, 133.2, 131.8, 124.8, 120.6, 120.4, 120.3, 120.1, 36.0, 35.8, 31.8, 31.8, 30.0, 29.7, 14.7, 14.3. HRMS m/z of $[M+H]^+$ calculated 436.300, obtained 436.304.

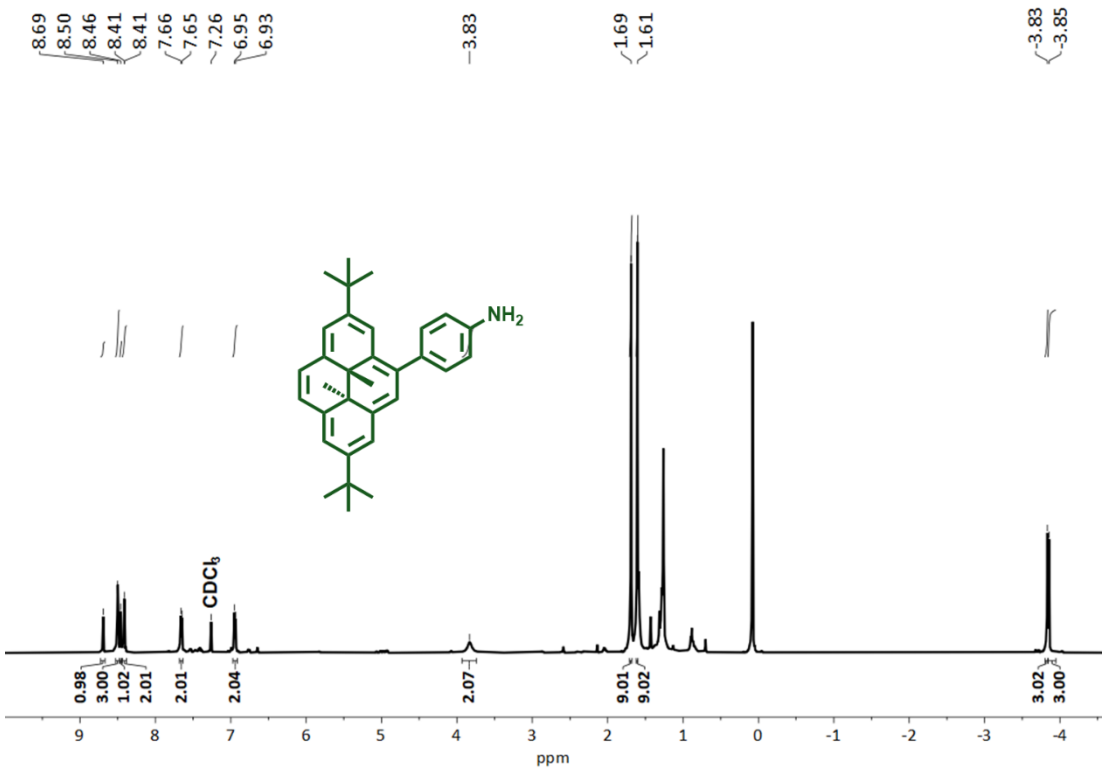


Fig. S1. ^{1}H NMR ($CDCl_3$, 500MHz) spectrum of compound **3**.

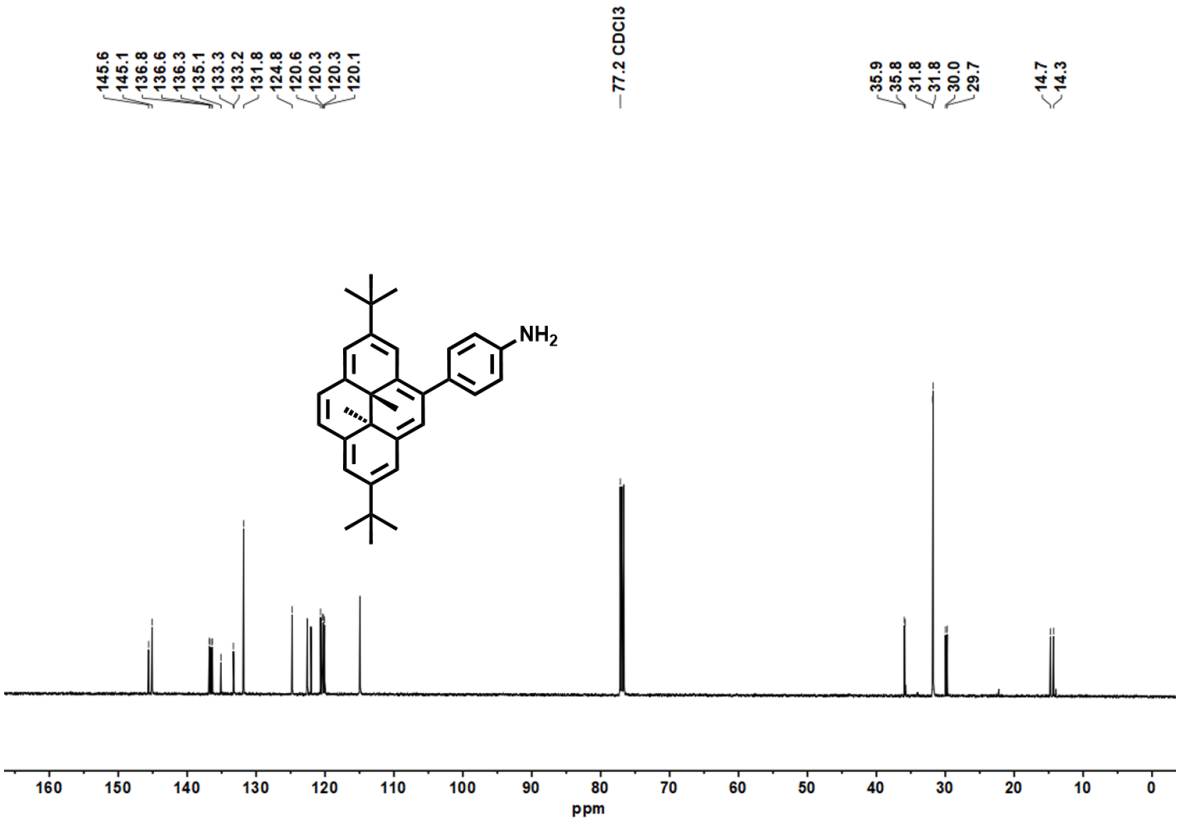


Fig. S2. ^{13}C {^{1}H} NMR ($CDCl_3$, 125MHz) spectrum of compound **3**.

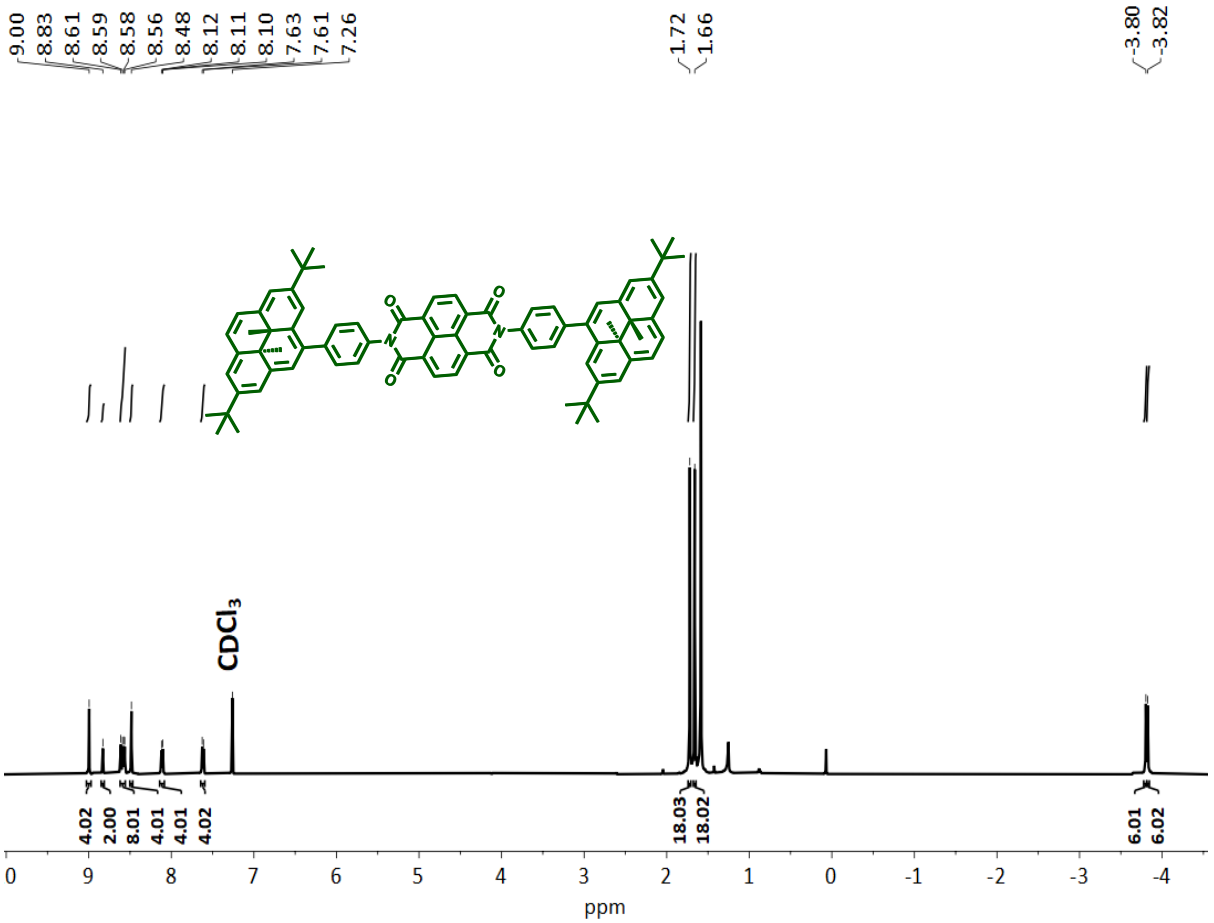


Fig. S3. ^{1}H NMR ($CDCl_3$, 500MHz) spectrum of compound **1*c***.

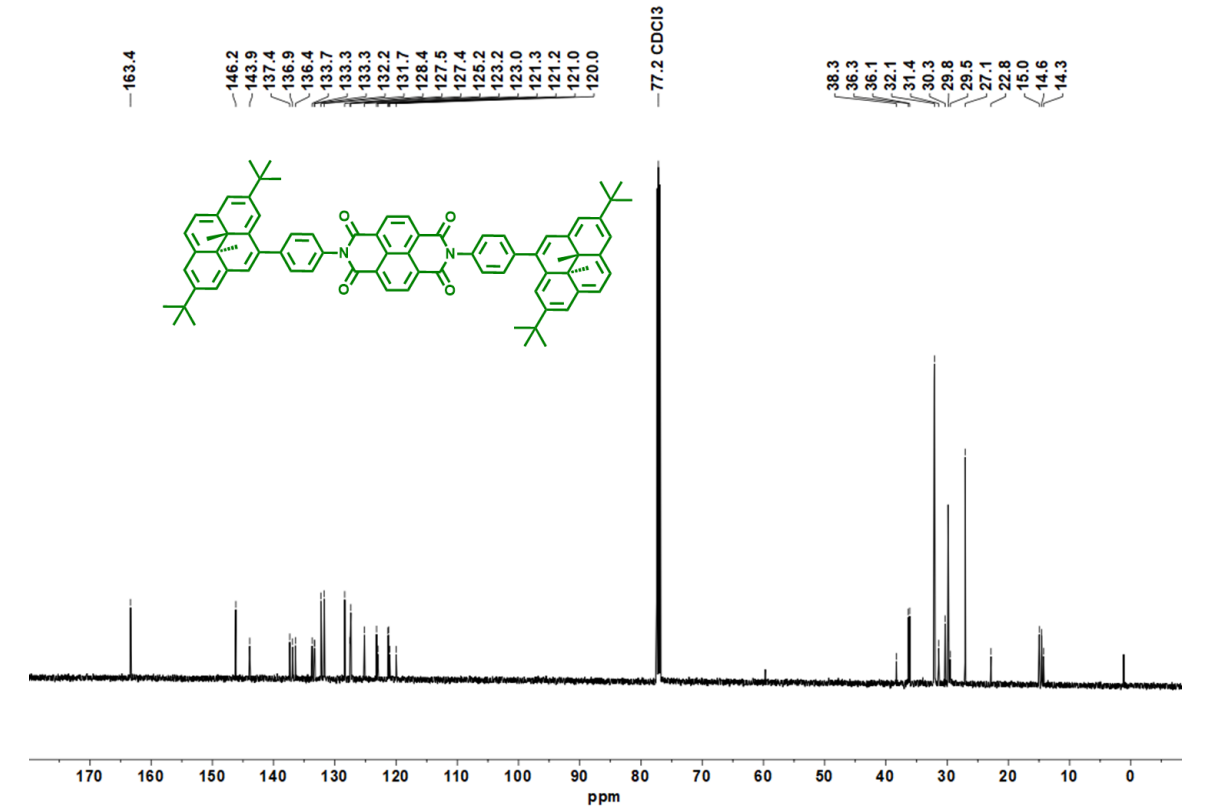


Fig. S4. ^{13}C {^{1}H} NMR ($CDCl_3$, 125MHz) spectrum of compound **1*c***.

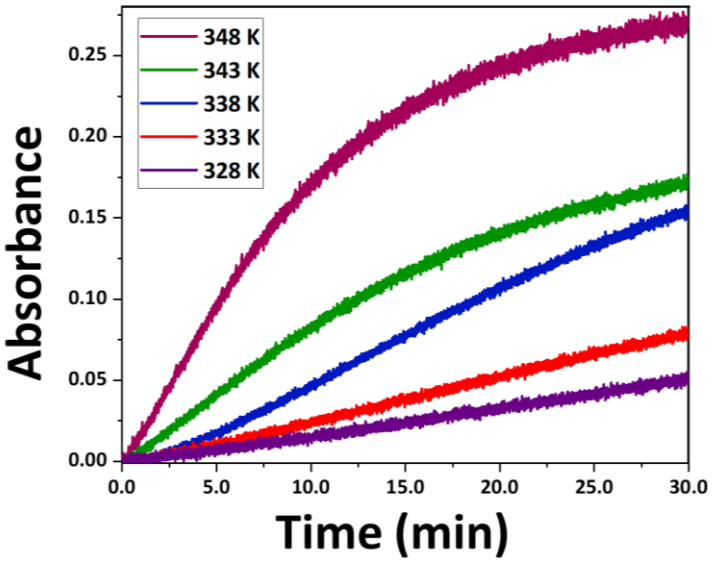


Fig. S5. Kinetics of thermal reversal at different temperatures.

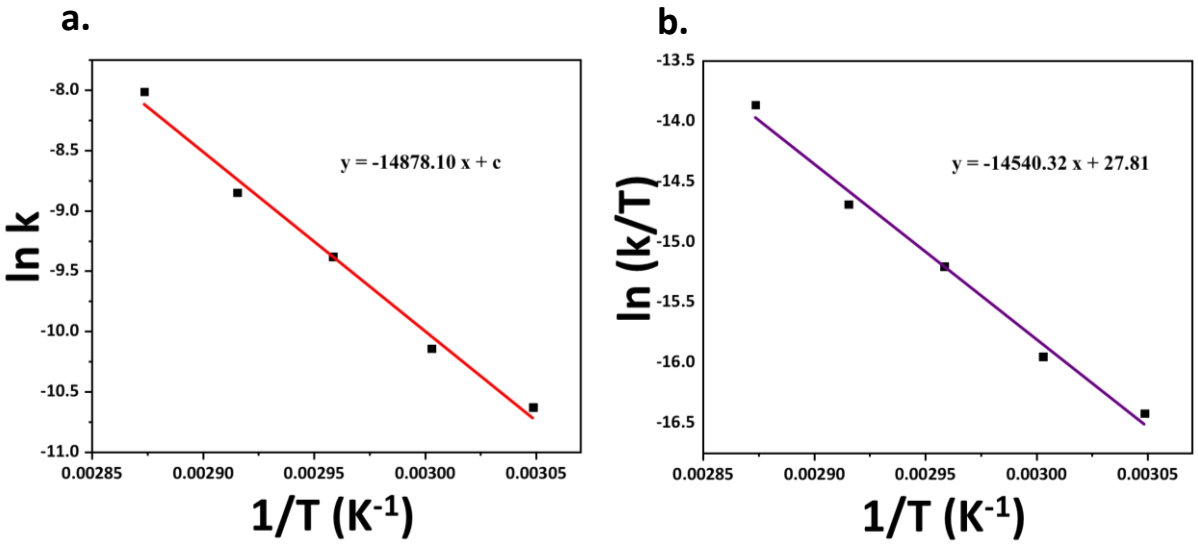


Fig. S6. a) Arrhenius plot and b) Eyring plot for the kinetics of thermal reversal.

Table S1: Thermodynamic parameters

The energy of activation (E_a) for CPD→DHP thermal reversal ($kcalmol^{-1}$)	Change in enthalpy ($\Delta H^{\neq}$) for CPD→DHP thermal reversal ($kcalmol^{-1}$)	Change in entropy ($\Delta S^{\neq}$) for CPD→DHP thermal reversal ($calK^{-1}mol^{-1}$)	Half-life ($t_{1/2}$) at 298 K (day)
29.4	**28.7**	**8.0**	**34**

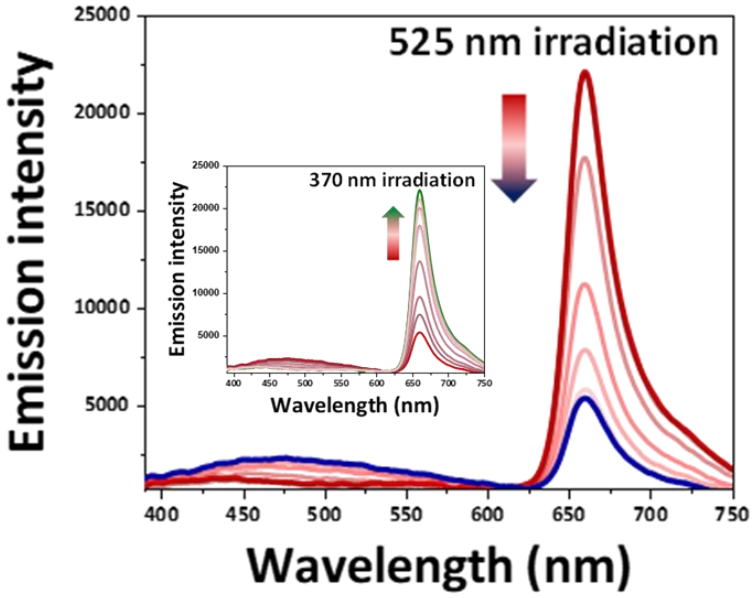


Fig. S7. Emission spectral change of **1***c*$^{\cdot-}$ on irradiation with 525 nm light. Lowering of the emission intensity of **1***c*$^{\cdot-}$ under irradiation 525 nm light (**1***c*$^{\cdot-}$→**1***o*). Regeneration of the emission intensity by 370 nm exposure to the same sample (**1***o* → **1***c*$^{\cdot-}$) (inset).

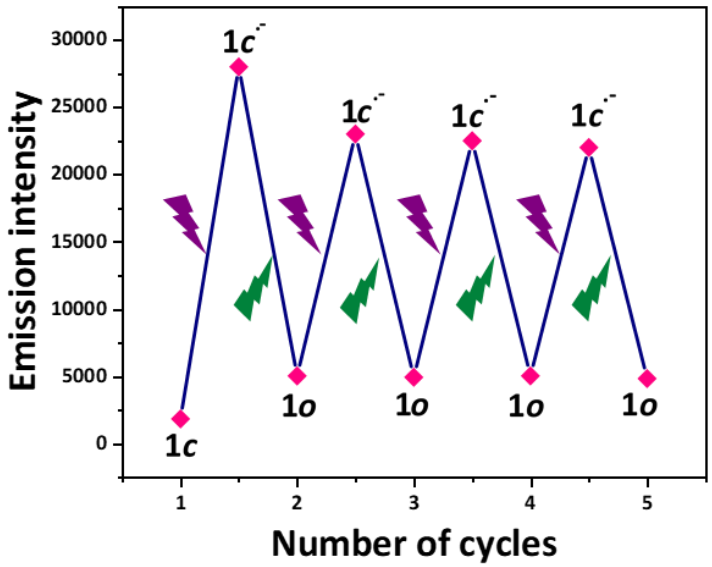


Fig. S8. Multiple cycle of the change in emission under repeated irradiation of 370 nm and 525 nm light.

The role of amine in radical formation:

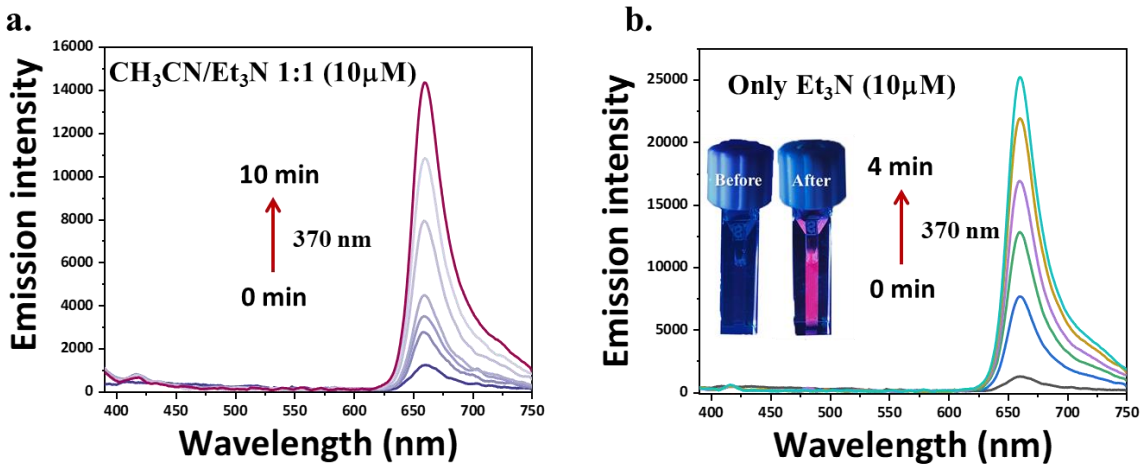


Fig. S9. Emission spectral changes of 1c in different amine-based solvents under 370 nm light exposure a) acetonitrile/triethylamine 1:1 (v/v). b) pure triethylamine; photographs of emission colour change are also inserted.

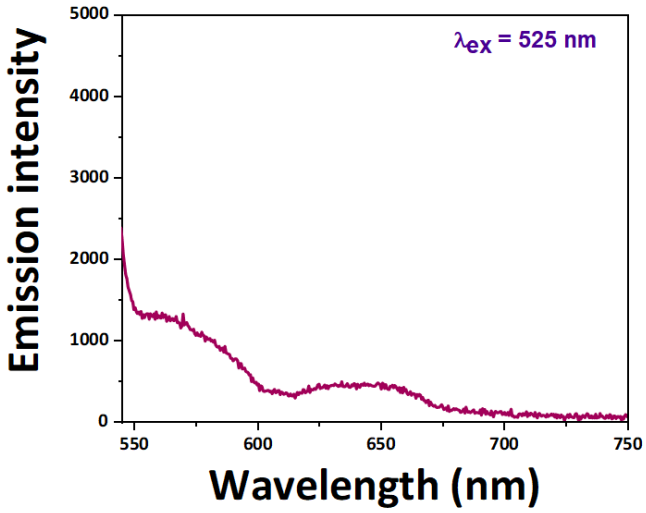


Fig. S10. Emission spectra of **1*c***; λex = 525 nm.

Control study with parent DHP and NDA under 370 nm exposure:

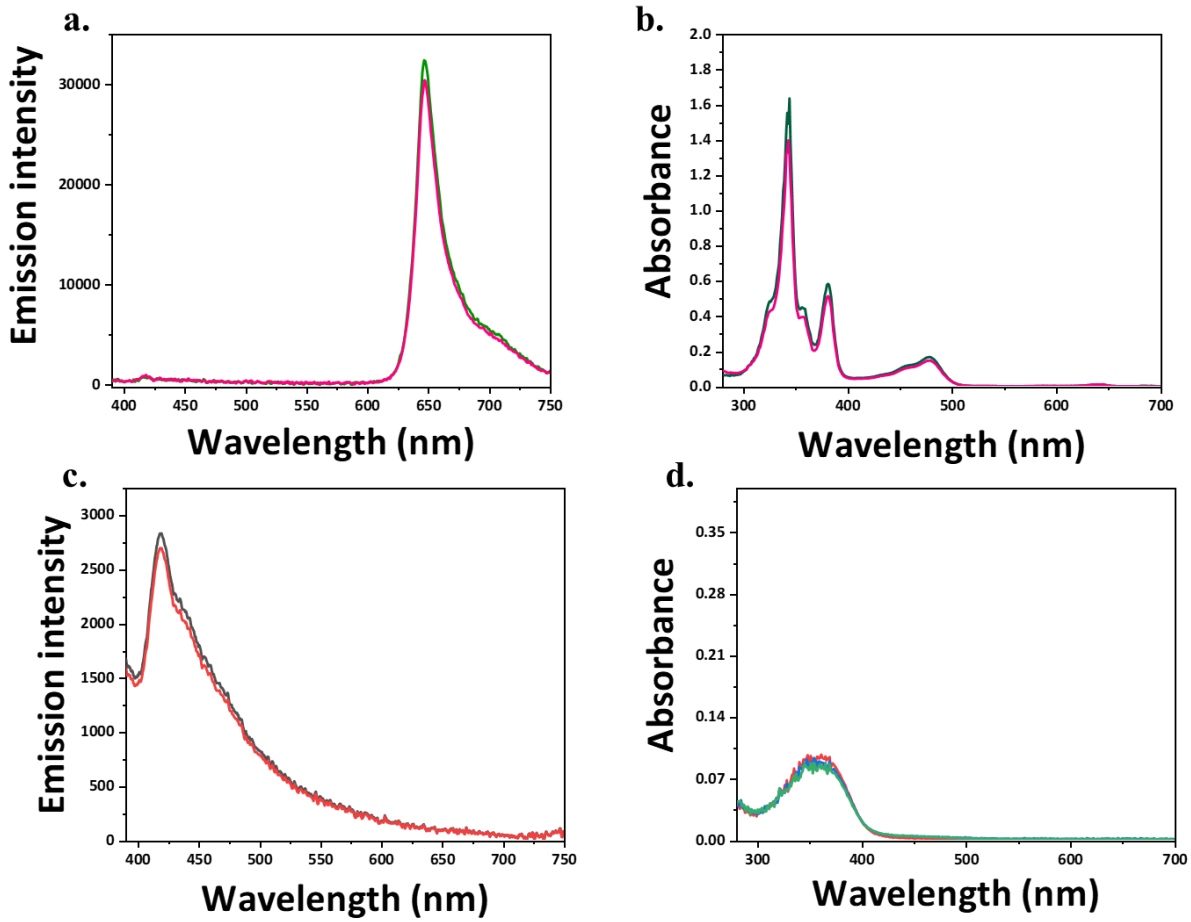


Fig. S11. Control study with parent DHP and NDA. a) emission and b) UV-vis spectral changes of DHP on irradiation with 370 nm light (0-10 min). c) emission and d) UV-vis spectra changes of NDA on irradiation with 370 nm light (0-10 min).

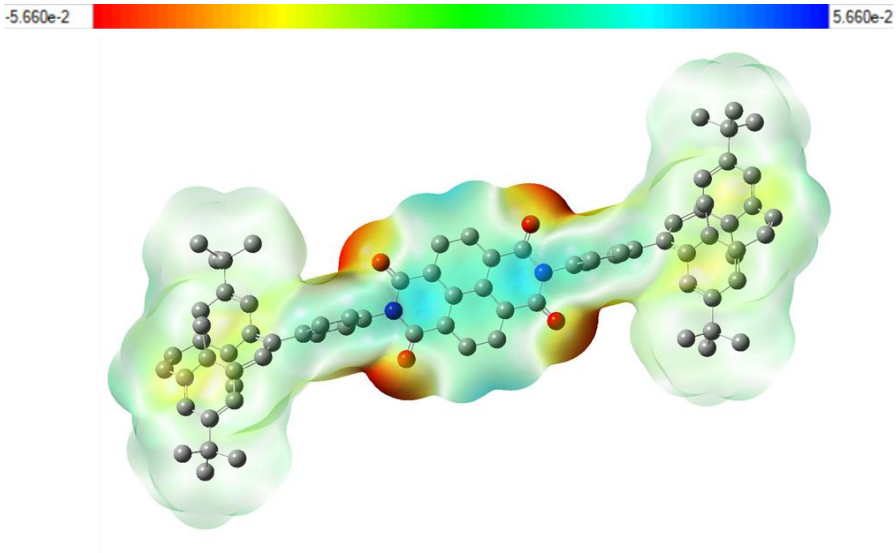


Fig. S12. Electrostatic potential surface analysis of **1c**.

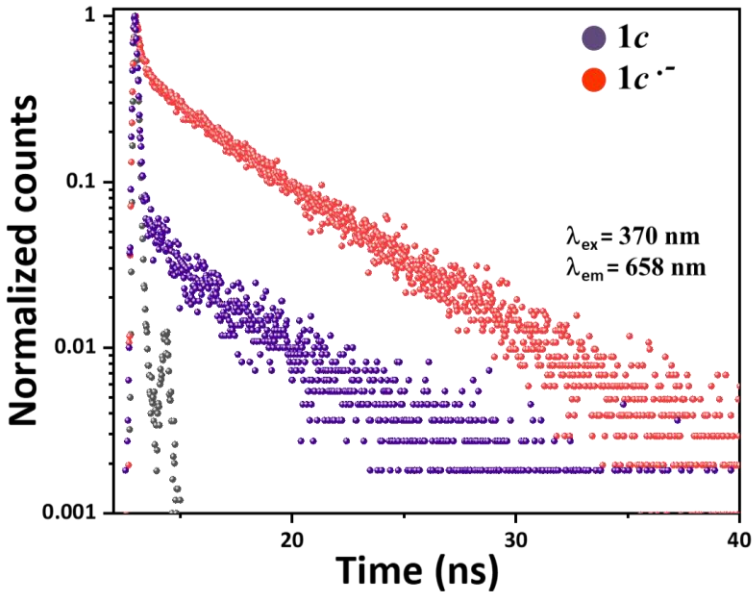


Fig. S13. Photo-luminescence decay life time of **1*c*** and **1c**$^{\bullet-}$.

Table S2:

Compound	Average Fluorescence Lifetime
1*c*	**0.069 ns**
1*c*$^{\bullet-}$	**0.81 ns**

Reduction of 1*c* with TDAE:

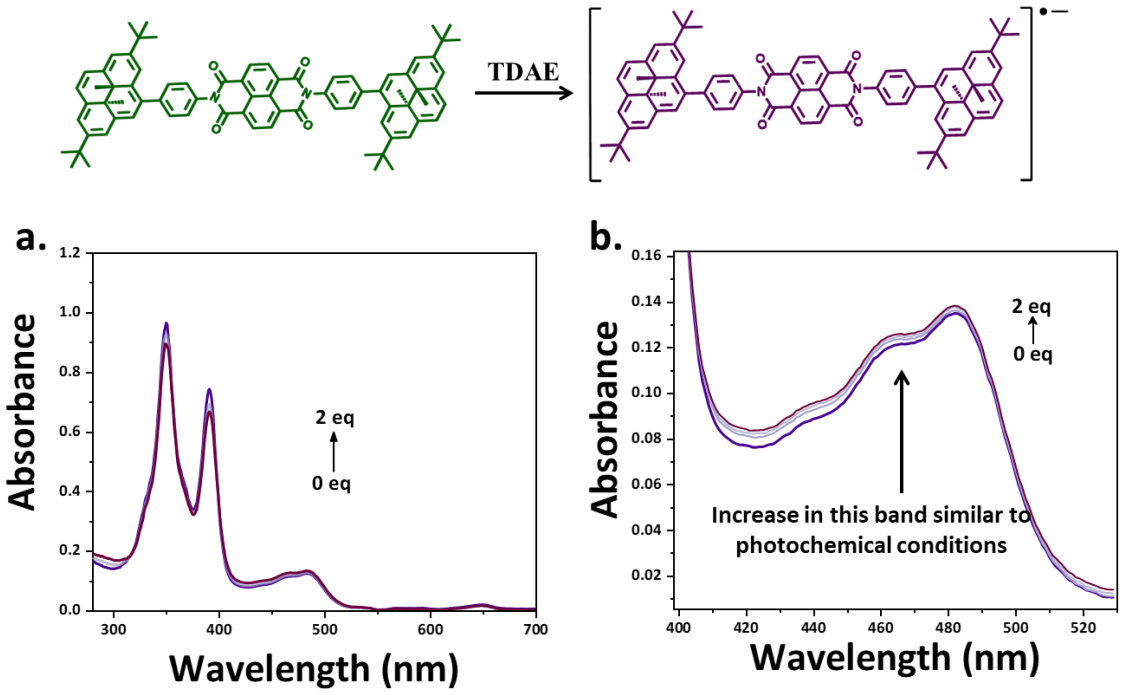


Fig. S14. a) Radical anion generation upon addition of TDAE (10 μM solution in CH_3CN). b) Increase in the absorbance at 484 nm.

Aggregation study at low temperature:

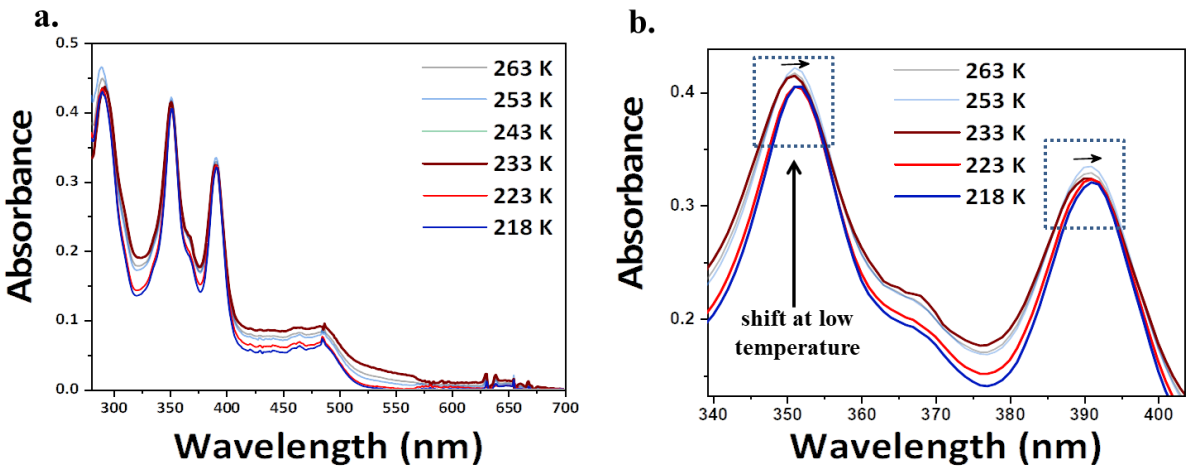


Fig. S15. a) UV-vis spectral shift of **1***c*$^{\bullet-}$ upon decreasing temperature (10 μM solution in DMF). b) Regions at 350 nm and 390 nm are zoomed in, the small arrow indicates the direction of the shift.

DDQ oxidation of 1c$^{\bullet-}$:

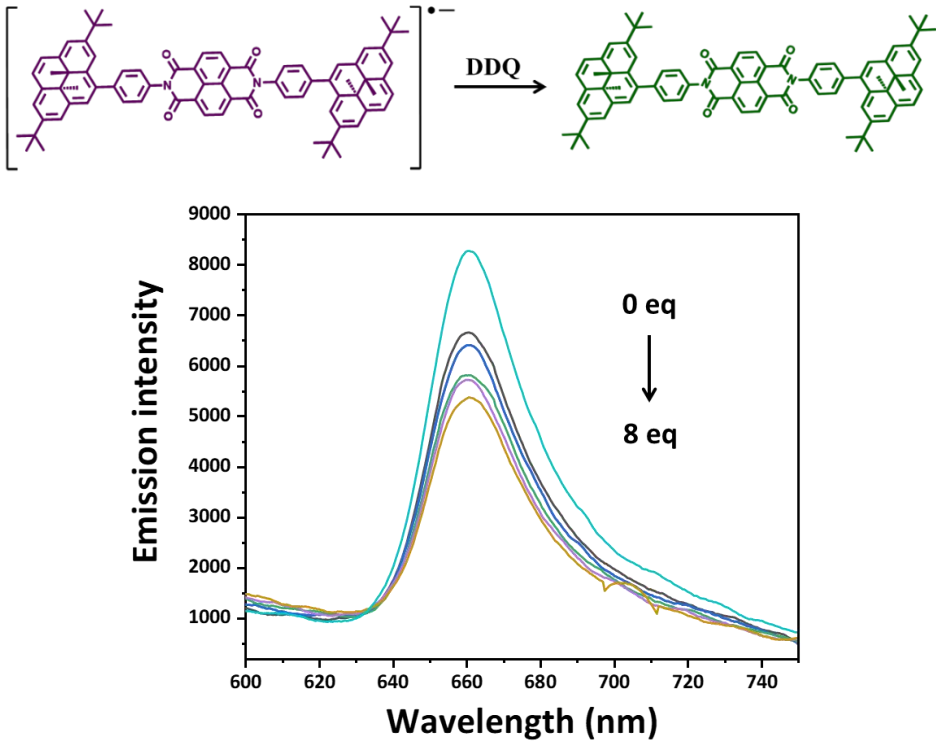


Fig. S16. Decrease of the emission intensity of **1c**$^{\bullet-}$ upon addition of DDQ (10 μM solution in CH_3CN)

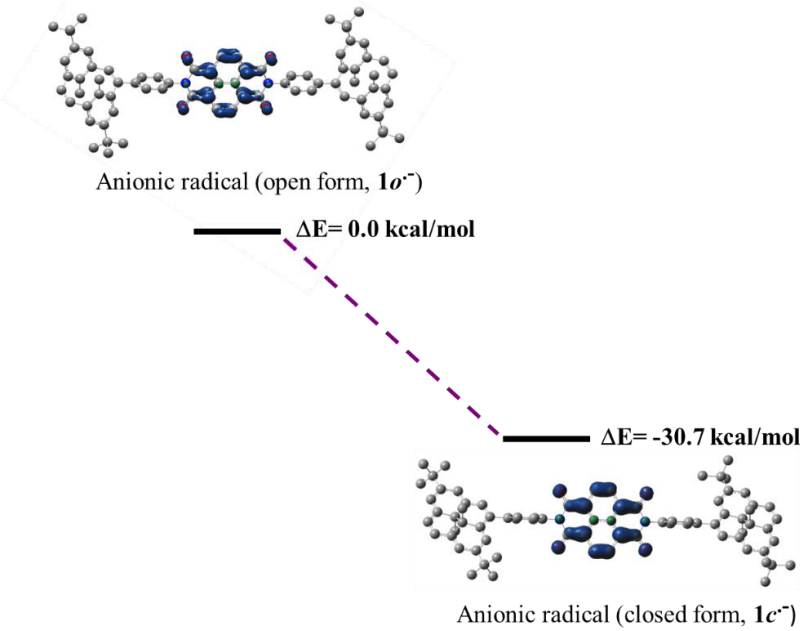


Fig. S17. Energy levels of the radical anions for both open and closed form (**1c**$^{\bullet-}$).

Spectral simulation of 1c and 1c$^{\cdot-}$:

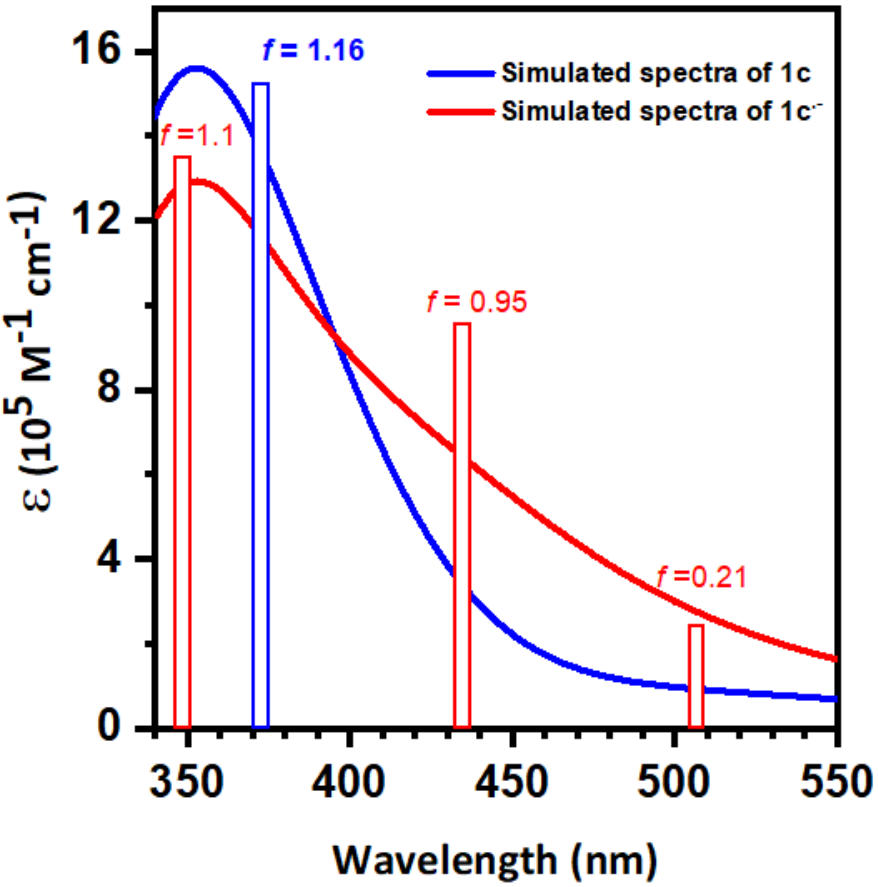


Fig. S18. TD DFT simulated spectra of **1*c*** and **1*c***$^{\cdot-}$. Note the predicted increase in absorption in the 430-500 nm region is consistent with the experimental observation. The transitions with having oscillation strength (f = 0.1) are plotted using the bar graph. Note the absence of any major transition (f > 0.1) >400 nm region for the neutral closed form.

MO analysis of 1c:

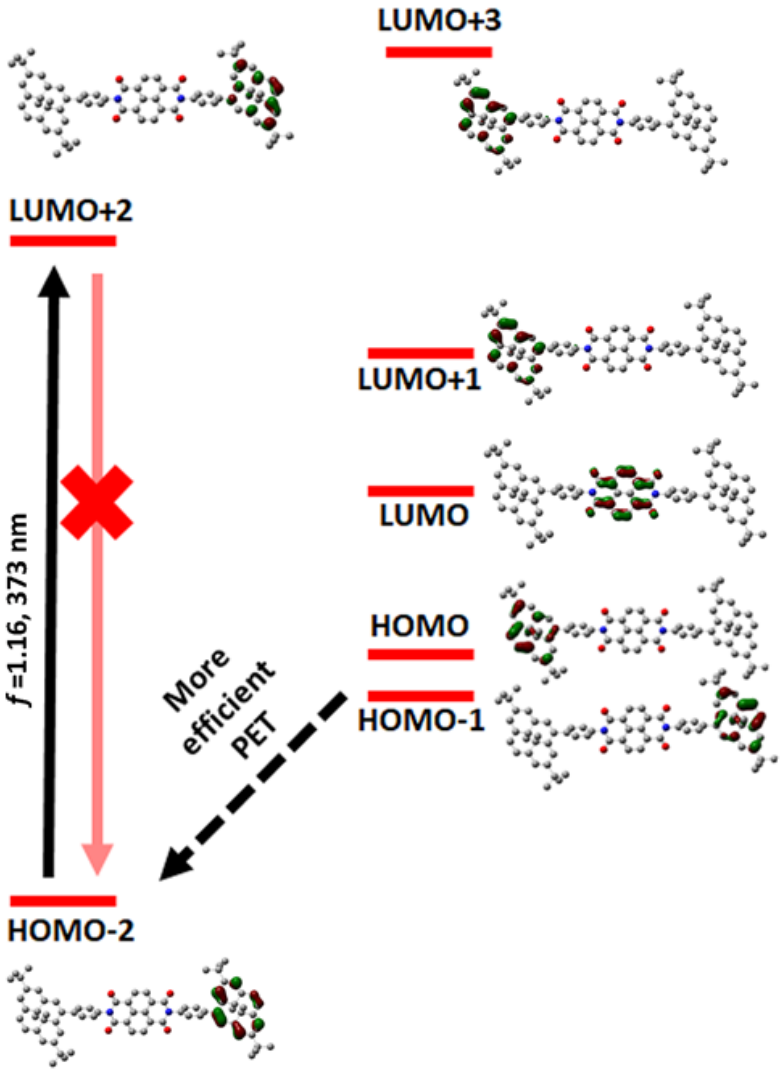


Fig. S19. MO analysis of the TD DFT predicted transitions in **1*c*** reveals the possibility of local electron transfer inhabiting fluorescence.

Absorbance at 525 nm of 1*c*:

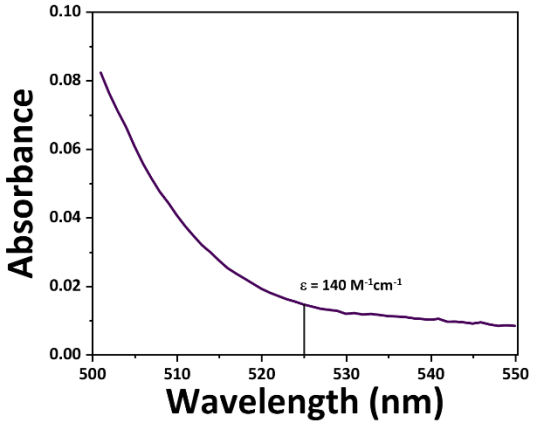


Fig. S20. Absorbance at 525 nm of **1*c*** (10μM in $CHCl_3$:CH_3CN 1:1, degassed with N_2)

Table S3: Optimized coordinates
Neutral DHP−NDI−DHP (1*c*):

C	13.80340600	2.01055900	-0.15584500
C	14.38236400	0.73689300	-0.11085300
C	13.60566000	-0.42047900	0.04236100
C	12.12782900	-0.22276900	0.35586300
C	11.55892500	0.95512700	-0.46124000
C	12.41316300	2.19456600	-0.22075900
C	11.28794000	-1.46522700	0.11822700
C	9.90208700	-1.28754500	0.02370800
C	9.28429500	-0.02246400	-0.03812000
C	10.07479600	1.15201700	-0.14972100
C	9.57895900	2.45473500	-0.09561000
C	10.39890600	3.60107200	-0.15577100
C	11.79710800	3.44326700	-0.19588000
C	14.12838300	-1.71473000	0.05897900
C	13.31704800	-2.86316100	0.13521700
C	11.91385500	-2.71005700	0.12521000
C	7.79489300	0.01984400	-0.01833600
C	7.06060800	0.69981100	-1.00686000
C	5.66733300	0.69236600	-1.00180200
C	4.98423700	0.00006300	-0.00245800
C	5.68700700	-0.68707100	0.98591200
C	7.08063600	-0.67685000	0.97258600
N	3.53631500	-0.00665000	0.00621700
C	2.89168400	-1.06213400	-0.66656000
C	1.40683900	-1.05268600	-0.64962200
C	0.71139200	-0.01541300	0.01814500
C	1.40601800	1.02562600	0.68088200
C	2.89081100	1.04428500	0.68520100
C	0.70500800	-2.06092100	-1.29104000
C	-0.70197100	-2.06432900	-1.28655600
C	-1.40456300	-1.05962300	-0.64044800

C	-0.70988900	-0.01904700	0.02297100
C	-1.40530800	1.01819700	0.69078900
C	-0.70351000	2.02613100	1.33271200
C	0.70345000	2.02993900	1.32761800
C	-2.88940200	-1.07602300	-0.64821900
N	-3.53489400	-0.02425500	0.02948800
C	-2.89013100	1.02882500	0.70595300
C	-4.98281700	-0.02487000	0.02956300
C	-5.67572400	0.68244600	-0.95159000
C	-7.06929600	0.68028700	-0.94690300
C	-7.79394900	-0.02879900	0.02781600
C	-7.06934100	-0.72986000	1.00902500
C	-5.67600500	-0.72994400	1.01289600
C	-9.28247300	0.02236200	0.03853300
C	-10.08142300	-1.14922100	0.13392900
C	-11.56569300	-0.94605800	0.44184200
C	-12.12364800	0.24288200	-0.36688100
C	-11.27697800	1.47766800	-0.11541700
C	-9.89387800	1.29109400	-0.01496000
C	-12.42647400	-2.17767500	0.18678500
C	-13.81424800	-1.98469100	0.11590500
C	-14.38661600	-0.70776300	0.08052200
C	-13.60157900	0.44724300	-0.05690000
C	-9.59873400	-2.45293600	0.06690300
C	-10.42669300	-3.59850700	0.11475900
C	-11.82075600	-3.43456900	0.15345700
C	-14.11074700	1.74378700	-0.06238400
C	-13.29110200	2.89144600	-0.12716600
C	-11.89237100	2.73114700	-0.11534700
O	3.53866200	1.91768500	1.24329400
O	3.54013000	-1.93148200	-1.23023300
O	-3.53850900	1.89772800	1.27036900

O	-3.53727200	-1.94772600	-1.20892700
C	-13.95433600	4.28206300	-0.13860500
C	-14.79097800	4.47196800	1.15048100
C	-12.92779700	5.42873900	-0.21341700
C	-14.88445200	4.39193800	-1.37148200
C	-9.76808400	-4.98986200	0.04947300
C	-8.98545600	-5.13507300	-1.27891600
C	-8.78900500	-5.14823100	1.23848600
C	-10.79548400	-6.13581600	0.12435800
C	9.81007800	5.02458200	-0.10762500
C	8.26967400	5.03196600	-0.06903600
C	10.32352200	5.75948400	1.15502900
C	10.25960800	5.80276400	-1.36860000
C	13.91177700	-4.28430600	0.15683200
C	15.45243900	-4.28254200	0.17875700
C	13.41689600	-5.02511600	1.42312000
C	13.45115400	-5.06079400	-1.10123900
C	11.62866900	0.69366200	-2.00731800
C	12.05611200	0.04503300	1.90120800
C	-11.63970500	-0.69815400	1.98990300
C	-12.04797300	-0.01172000	-1.91427500
H	14.44630600	2.88865400	-0.16219400
H	15.46508000	0.64002900	-0.16394200
H	9.26967600	-2.17260200	-0.00225500
H	8.51410500	2.58690400	0.04635000
H	12.43501300	4.32281100	-0.14495300
H	15.20410600	-1.82314100	-0.03831700
H	11.28337300	-3.59493100	0.07500800
H	7.58681600	1.22406500	-1.79833200
H	5.11098600	1.21357800	-1.77493200
H	5.14672900	-1.22126100	1.76157800
H	7.62543900	-1.20578900	1.74897500

H	1.25489300	-2.84661200	-1.79677000
H	-1.25125800	-2.85260100	-1.78890900
H	-1.25342100	2.81171700	1.83857300
H	1.25275000	2.81856200	1.82940400
H	-5.12764600	1.22620800	-1.71503900
H	-7.60610100	1.22499300	-1.71792200
H	-7.60323400	-1.26357000	1.78894200
H	-5.12750200	-1.26667400	1.78099700
H	-9.25688700	2.17244400	0.02435700
H	-14.46209500	-2.85921100	0.10883400
H	-15.46904600	-0.60539500	0.12751700
H	-8.53331300	-2.59697600	-0.07620900
H	-12.46803800	-4.30401800	0.09523300
H	-15.18734800	1.86516800	0.03450400
H	-11.25203900	3.60577400	-0.05854300
H	-15.27022800	5.45849400	1.14737300
H	-15.58077000	3.71932000	1.24252000
H	-14.15617200	4.40586300	2.04170700
H	-13.45487600	6.38871800	-0.24778100
H	-12.30397300	5.35994500	-1.11184500
H	-12.26821400	5.44689800	0.66151800
H	-15.66827800	3.62751800	-1.36108600
H	-15.37407100	5.37320200	-1.38996000
H	-14.31571900	4.27869600	-2.30184100
H	-8.51066900	-6.12239700	-1.33076100
H	-9.65585500	-5.03510100	-2.14041000
H	-8.19665500	-4.38203000	-1.37620100
H	-8.30410800	-6.13126600	1.20063700
H	-9.31888900	-5.06771800	2.19482500
H	-8.00179300	-4.38733400	1.22461700
H	-11.48871700	-6.12179700	-0.72421900
H	-10.27130300	-7.09778000	0.10470500

H	-11.38352100	-6.09678300	1.04837800
H	7.91017000	6.06700600	-0.06774900
H	7.83650200	4.53121600	-0.94231400
H	7.87894000	4.54761000	0.83298100
H	9.91334300	6.77596000	1.19326100
H	11.41528300	5.84101800	1.16738900
H	10.01390800	5.23416000	2.06597500
H	9.89474300	5.31503900	-2.28009500
H	9.85911300	6.82356300	-1.34592100
H	11.35004900	5.87341700	-1.43812300
H	15.81807300	-5.31441900	0.22450800
H	15.87526800	-3.82364900	-0.72204600
H	15.84720100	-3.75101600	1.05210400
H	13.82406700	-6.04318500	1.44903000
H	12.32500900	-5.10144600	1.45167200
H	13.74229100	-4.50611500	2.33229500
H	13.79589900	-4.56365200	-2.01536800
H	13.86470800	-6.07656500	-1.09045800
H	12.36091100	-5.14626700	-1.15463200
H	11.03698300	-0.18191100	-2.28779900
H	11.22361400	1.56458500	-2.53126500
H	12.66052900	0.54456500	-2.33675700
H	12.64309200	0.92491300	2.17778900
H	11.02277300	0.19139900	2.22801600
H	12.46388200	-0.82155300	2.42987100
H	-11.24785600	-1.57878000	2.50764300
H	-11.03854600	0.16724900	2.28153300
H	-12.67129400	-0.53918900	2.31561700
H	-11.01495100	-0.16820500	-2.23744800
H	-12.64470900	-0.88140000	-2.20192500
H	-12.44243600	0.86468900	-2.43681200

Anionic [DHP−NDI−DHP]$^{\bullet-}$ (1*c*$^{\bullet-}$):

C	13.69549700	2.03157800	-0.14655500
C	14.29226500	0.74580700	-0.12517700
C	13.53631300	-0.39262800	0.03290900
C	12.06482200	-0.21540500	0.35450300
C	11.48326000	0.95765500	-0.44593800
C	12.32962800	2.19468500	-0.20780500
C	11.24178900	-1.45849400	0.10962100
C	9.83482000	-1.28590800	0.04015800
C	9.22207100	-0.05174100	-0.00961900
C	10.01272300	1.14522800	-0.11076900
C	9.50769900	2.41492500	-0.03011100
C	10.31983400	3.58759300	-0.11493200
C	11.68978100	3.45186700	-0.18519900
C	14.07317000	-1.70102800	0.05383200
C	13.28056800	-2.82775800	0.10574000
C	11.85792700	-2.67862000	0.08578000
C	7.73492700	-0.00132100	0.00400900
C	7.01502400	0.67687600	-0.98634400
C	5.62700300	0.67372200	-0.98852900
C	4.93333000	-0.00667700	0.00446800
C	5.62845200	-0.68679500	0.99498900
C	7.01746500	-0.68436400	0.99108500
N	3.49539200	-0.00669000	0.00495900
C	2.85630500	-1.07497400	-0.64678200
C	1.40330500	-1.05862300	-0.63578800
C	0.71529600	-0.00498200	0.00396400
C	1.40413200	1.04777200	0.64428300
C	2.85712500	1.06251800	0.65593100
C	0.68797900	-2.09411500	-1.26475100
C	-0.68858400	-2.09317200	-1.26540800
C	-1.40308200	-1.05665100	-0.63720100

C	-0.71423700	-0.00395600	0.00321400
C	-1.40223000	1.04976300	0.64285000
C	-0.68691200	2.08516600	1.27196300
C	0.68964800	2.08420800	1.27263700
C	-2.85607500	-1.07094900	-0.64957400
N	-3.49432500	-0.00134200	0.00076400
C	-2.85522000	1.06659100	0.65308000
C	-4.93224100	0.00030800	-0.00121200
C	-5.62460000	0.68115700	-0.99320700
C	-7.01355600	0.68072300	-0.99203300
C	-7.73413200	-0.00094900	-0.00610600
C	-7.01682800	-0.67984700	0.98589400
C	-5.62880400	-0.67873300	0.99069200
C	-9.22070300	0.05119100	0.00434200
C	-10.01281200	-1.14493900	0.11517700
C	-11.48258700	-0.95319900	0.45303400
C	-12.06441700	0.21286000	-0.35742300
C	-11.23972700	1.45725700	-0.12765800
C	-9.83404800	1.28483100	-0.05656900
C	-12.33115800	-2.19132800	0.22897700
C	-13.69619800	-2.02688700	0.16776400
C	-14.29257900	-0.74136200	0.13547800
C	-13.53479700	0.39550100	-0.03372500
C	-9.51454600	-2.41493700	0.04113500
C	-10.32895000	-3.58900800	0.14020900
C	-11.69593700	-3.45433200	0.21705000
C	-14.06404300	1.70321400	-0.06581600
C	-13.27066300	2.83231600	-0.13480300
C	-11.85190000	2.68270500	-0.11762600
O	3.53205300	1.94019000	1.19300300
O	3.53046700	-1.95307100	-1.18408200
O	-3.52938700	1.94491700	1.18999500

O	-3.53102600	-1.94844800	-1.18690800
C	-13.93105300	4.21901400	-0.16004400
C	-14.76158700	4.42092900	1.12086100
C	-12.90816500	5.35895100	-0.24717800
C	-14.85699100	4.31739900	-1.38634200
C	-9.63395000	-4.95329800	0.09446700
C	-8.88866500	-5.11007700	-1.24446900
C	-8.62334000	-5.04687300	1.25311700
C	-10.62118400	-6.11824300	0.22905500
C	9.69996600	4.99258700	-0.06616800
C	8.16758700	4.96226000	0.00148200
C	10.21672200	5.74463300	1.17427900
C	10.10361200	5.76781400	-1.33393400
C	13.86184000	-4.24499700	0.11847100
C	15.39441700	-4.25039300	0.15016400
C	13.35513100	-4.98888500	1.36825600
C	13.40673300	-5.00204400	-1.14343600
C	11.53516000	0.70539000	-1.98347400
C	11.99757500	0.03720700	1.89223200
C	-11.53005600	-0.68582200	1.98802000
C	-12.00186200	-0.05499100	-1.89289600
H	14.33325800	2.91200800	-0.13174500
H	15.37325800	0.66076900	-0.20491900
H	9.21439400	-2.17861100	0.02918600
H	8.44657900	2.53542000	0.14056800
H	12.32237900	4.33570300	-0.16546300
H	15.15117700	-1.79643100	-0.02029800
H	11.23730600	-3.56726300	0.01019200
H	7.54963800	1.19971800	-1.77243700
H	5.07650200	1.19472900	-1.76503300
H	5.08034500	-1.21369400	1.76919200
H	7.55712900	-1.21097500	1.77174000

H	1.24779500	-2.88790000	-1.74572600
H	-1.24902800	-2.88619100	-1.74691600
H	-1.24673000	2.87898600	1.75287800
H	1.25010000	2.87724700	1.75410300
H	-5.07427400	1.20696700	-1.76657800
H	-7.55082300	1.20745500	-1.77424500
H	-7.55350900	-1.20083500	1.77182600
H	-5.08058300	-1.20011300	1.76855600
H	-9.21354800	2.17760500	-0.05199700
H	-14.33477600	-2.90689100	0.16080200
H	-15.37344700	-0.65473000	0.21445100
H	-8.45312000	-2.54530300	-0.13437800
H	-12.33325600	-4.33214500	0.21197500
H	-15.14310600	1.80780300	0.01418700
H	-11.22516600	3.56537000	-0.05487500
H	-15.23703500	5.40781400	1.11120800
H	-15.55169400	3.67090500	1.21640800
H	-14.12752500	4.35853400	2.01128000
H	-13.43535100	6.31682900	-0.29452200
H	-12.28376500	5.27894800	-1.14269400
H	-12.25132600	5.38861000	0.62782700
H	-15.64230600	3.55669400	-1.36393300
H	-15.34188200	5.29924400	-1.41653300
H	-14.29065300	4.18972000	-2.31474000
H	-8.38404000	-6.08150600	-1.28177400
H	-9.58578300	-5.05678100	-2.08698800
H	-8.12838100	-4.33680900	-1.38595400
H	-8.10937600	-6.01379100	1.22783800
H	-9.12935900	-4.95634100	2.21991500
H	-7.86166400	-4.26383400	1.19687500
H	-11.33822400	-6.14291900	-0.59749000
H	-10.07237000	-7.06498900	0.21820400

H	-11.18152900	-6.06865400	1.16805000
H	7.78414900	5.98727500	-0.00177300
H	7.73079000	4.44186900	-0.85685100
H	7.80642400	4.47989900	0.91520200
H	9.78064700	6.74869000	1.21644500
H	11.30479800	5.85382000	1.16015200
H	9.94232600	5.21680300	2.09344700
H	9.73757200	5.26283400	-2.23389900
H	9.67641500	6.77632500	-1.31274000
H	11.18931400	5.86599600	-1.42112000
H	15.75514500	-5.28301300	0.18541500
H	15.82256200	-3.78148400	-0.74129200
H	15.78367400	-3.73108500	1.03157500
H	13.75319400	-6.00915200	1.38705100
H	12.26372400	-5.05671000	1.38939000
H	13.67919100	-4.48089100	2.28250400
H	13.76233600	-4.49944000	-2.04875000
H	13.81237500	-6.01946900	-1.13801000
H	12.31773700	-5.08002200	-1.20645800
H	10.93782200	-0.16474100	-2.26495800
H	11.12885000	1.58040400	-2.49747900
H	12.56255400	0.55463600	-2.32190900
H	12.56671900	0.92723200	2.16885900
H	10.96557000	0.15741000	2.22997300
H	12.42899700	-0.82327500	2.40986600
H	-11.12839400	-1.55839600	2.50977700
H	-10.92658300	0.18297800	2.26033800
H	-12.55586500	-0.52496100	2.32667600
H	-10.97124900	-0.18566900	-2.23106400
H	-12.57780800	-0.94351100	-2.16003300
H	-12.42842500	0.80342900	-2.41792100

Neutral [CPD−NDI−CPD] (1*o*):

C	13.58805900	1.64894100	-1.05155400
C	14.21183000	0.65486400	-0.38793600
C	13.51927500	-0.48955700	0.26596600
C	12.33910100	-0.30153900	1.01114900
C	11.14538900	0.94990400	-1.08144700
C	12.12889900	1.94856900	-0.97532800
C	11.36137000	-1.30347900	0.90329100
C	9.90073600	-1.02850300	0.93350300
C	9.24812900	-0.03130800	0.28538700
C	9.97249700	1.13339000	-0.32690000
C	9.63351200	2.41601800	0.11229600
C	10.48062400	3.51214000	-0.07100200
C	11.76286700	3.22677400	-0.53727600
C	13.88099700	-1.77799800	-0.13141800
C	13.03890100	-2.87803300	0.06589600
C	11.74649300	-2.59099300	0.49948000
C	7.76183500	-0.01325200	0.27160900
C	7.07978300	0.45392900	-0.85832100
C	5.69369700	0.44313700	-0.91450600
C	4.96710100	-0.02402300	0.17253700
C	5.61865600	-0.47520800	1.31185000
C	7.00584800	-0.46466100	1.35959300
N	3.52598200	-0.02697900	0.12207600
C	2.90249400	-1.20010700	-0.32042900
C	1.42066200	-1.18870800	-0.37220600
C	0.71174100	-0.02988300	0.01268700
C	1.38618000	1.12978900	0.45299800
C	2.86747000	1.14355600	0.51874300
C	0.74364200	-2.30872000	-0.79694600
C	-0.66149100	-2.31018500	-0.85155000
C	-1.37169100	-1.19122900	-0.48173500

C	-0.69713100	-0.03080900	-0.04360900
C	-1.40597700	1.12878600	0.33906700
C	-0.72900500	2.24862300	0.76434800
C	0.67597700	2.24881800	0.82258100
C	-2.85318200	-1.20657900	-0.54302400
N	-3.51140200	-0.03325800	-0.15436300
C	-2.88759800	1.14211000	0.28187300
C	-4.95241500	-0.03496700	-0.20695700
C	-5.60005500	0.28202200	-1.39290200
C	-6.98702400	0.27303600	-1.44194700
C	-7.74754400	-0.03775200	-0.30856100
C	-7.06936500	-0.37110400	0.87010800
C	-5.68313600	-0.36603500	0.92610900
C	-9.23358700	-0.00690100	-0.32496700
C	-9.97142200	-1.06469200	0.44436100
C	-11.13151900	-0.76162900	1.17094700
C	-12.32558200	0.19765300	-1.06992200
C	-11.33490000	1.19224600	-1.10903500
C	-9.87764900	0.89792600	-1.10420700
C	-12.13195200	-1.75487400	1.21393900
C	-13.58639400	-1.42514300	1.25302000
C	-14.20113300	-0.52570300	0.45887500
C	-13.49864200	0.50476200	-0.35402600
C	-9.64802000	-2.40539200	0.18604300
C	-10.50557800	-3.44830100	0.52450100
C	-11.78491700	-3.08030400	0.95591100
C	-13.84307600	1.84146800	-0.14325900
C	-12.98889400	2.89110400	-0.49808100
C	-11.70198300	2.52854600	-0.89041900
O	3.49681600	2.11345400	0.89444500
O	3.56111600	-2.16974900	-0.64288500
O	-3.54574500	2.11515900	0.59490500

O	-3.48278600	-2.18001500	-0.90899300
C	-13.43850100	4.34649300	-0.33376700
C	-13.76384300	4.63168400	1.14339600
C	-12.36193100	5.33884900	-0.78872800
C	-14.69964700	4.58075300	-1.18435100
C	-10.14741600	-4.92557700	0.33407000
C	-11.07982800	-5.56058000	-0.71307800
C	-8.69982100	-5.11259000	-0.13519100
C	-10.31744800	-5.66024100	1.67585600
C	10.02912800	4.91686200	0.34169900
C	8.75870600	5.28658900	-0.44468300
C	9.71852500	4.94627200	1.84893000
C	11.09877800	5.97603400	0.05079700
C	13.50762100	-4.28925100	-0.30288300
C	14.76843600	-4.62818700	0.51216800
C	12.44190100	-5.34935100	-0.00110600
C	13.84199100	-4.35538900	-1.80389100
C	11.32486900	-0.25680300	-1.96482700
C	12.15885500	0.90382000	1.89371200
C	-11.29234000	0.55875800	1.87746200
C	-12.16569200	-1.12219500	-1.77465300
H	14.21498900	2.38251500	-1.55553300
H	15.29523200	0.59568600	-0.47498600
H	9.28632200	-1.82443000	1.34948300
H	8.69778200	2.54266200	0.64827400
H	12.52883000	3.99489400	-0.52691300
H	14.82411100	-1.90509200	-0.65626600
H	10.98645100	-3.36485300	0.49223900
H	7.64609300	0.82369800	-1.70659500
H	5.17426000	0.79692600	-1.79887700
H	5.04076000	-0.82050100	2.16269000
H	7.50798600	-0.79246900	2.26335300

H	1.30711900	-3.18721300	-1.08789700
H	-1.19892300	-3.19002100	-1.18467100
H	-1.29240700	3.12785400	1.05319900
H	1.21330900	3.12792100	1.15779500
H	-5.01905900	0.52121900	-2.27740700
H	-7.48527800	0.49258000	-2.37993600
H	-7.63888000	-0.63134700	1.75605300
H	-5.16693800	-0.61705600	1.84678500
H	-9.25680500	1.62225300	-1.62744700
H	-14.21964400	-2.07102100	1.85870700
H	-15.28295500	-0.43919700	0.54271500
H	-8.71493000	-2.61270100	-0.32472800
H	-12.55985200	-3.83656800	1.04918600
H	-14.78212800	2.05369000	0.36097300
H	-10.93243300	3.28571800	-0.99534500
H	-14.08577700	5.67151200	1.26684600
H	-14.56705100	3.98878100	1.51493600
H	-12.88374300	4.47137100	1.77480300
H	-12.74436600	6.36064500	-0.70142000
H	-12.07753800	5.17618700	-1.83328300
H	-11.45881400	5.27214500	-0.17386900
H	-15.51657500	3.91711000	-0.88590900
H	-15.04795100	5.61327800	-1.07196800
H	-14.49397500	4.40520700	-2.24543400
H	-10.82791300	-6.61740400	-0.85350100
H	-12.12952600	-5.50666200	-0.41013100
H	-10.98135200	-5.05651400	-1.68011300
H	-8.47334900	-6.18080100	-0.20969000
H	-7.98659700	-4.66744300	0.56594900
H	-8.53027100	-4.67074200	-1.12218000
H	-11.34300400	-5.58662000	2.04959200
H	-10.07803700	-6.72295800	1.56036400

H	-9.65078200	-5.24269000	2.43758200
H	8.40919500	6.28374900	-0.15563300
H	8.95406300	5.29427900	-1.52209400
H	7.94639400	4.57865700	-0.25530900
H	9.39505400	5.94874600	2.14975200
H	10.60560000	4.68536400	2.43543200
H	8.92093500	4.24623100	2.11410300
H	11.37148500	5.99499100	-1.00925500
H	10.71565900	6.96659900	0.31521400
H	12.00895400	5.80851600	0.63531800
H	15.12949800	-5.63003300	0.25528200
H	15.57843300	-3.91950000	0.31587600
H	14.55684700	-4.60849200	1.58634800
H	12.83707100	-6.34333800	-0.23301100
H	11.54003600	-5.20502500	-0.60438400
H	12.15217700	-5.34238700	1.05456300
H	14.63803000	-3.65583300	-2.07498500
H	14.17798400	-5.36262200	-2.07354200
H	12.96210100	-4.11704700	-2.41047000
H	10.53131800	-0.98690600	-1.80244700
H	11.25970900	0.07258100	-3.00896400
H	12.28576900	-0.75489500	-1.84223200
H	12.89563300	1.67589300	1.67285500
H	11.16332300	1.34210300	1.84137000
H	12.31915100	0.58590000	2.93161500
H	-11.24114300	0.37591900	2.95770100
H	-10.48242600	1.24313800	1.62268600
H	-12.24162800	1.05440600	1.67825700
H	-11.17343000	-1.55843100	-1.67002700
H	-12.90678900	-1.84795900	-1.44045000
H	-12.33416000	-0.95222200	-2.84553200

Anionic [CPD−NDI−CPD]$^{\bullet-}$:

C	13.56681900	1.66481700	-1.03375200
C	14.19102000	0.66618600	-0.37736600
C	13.49923300	-0.48550100	0.26441100
C	12.31628000	-0.30651900	1.00754000
C	11.12560200	0.96101700	-1.07698100
C	12.10679800	1.96070800	-0.95924400
C	11.34043200	-1.30882700	0.88705600
C	9.87902900	-1.03671400	0.91671800
C	9.22518200	-0.03546700	0.27599300
C	9.94991800	1.13531400	-0.32456600
C	9.60701000	2.41368800	0.12399000
C	10.45269100	3.51297400	-0.04654500
C	11.73705600	3.23433300	-0.51099900
C	13.86496600	-1.76948500	-0.14350700
C	13.02416200	-2.87270900	0.04118800
C	11.72979700	-2.59185900	0.47301800
C	7.73874100	-0.01689200	0.26184700
C	7.05540700	0.45795300	-0.86396100
C	5.66895800	0.44686000	-0.91862300
C	4.93700000	-0.02657800	0.16296200
C	5.59446500	-0.48512200	1.29683900
C	6.98181400	-0.47623500	1.34568700
N	3.50013700	-0.02884000	0.11399500
C	2.87782700	-1.21617600	-0.30696200
C	1.42552400	-1.20073100	-0.35156900
C	0.72175000	-0.03347300	0.01576100
C	1.39389200	1.13570300	0.43291600
C	2.84567600	1.15579700	0.49223400
C	0.72667000	-2.35063100	-0.76245800
C	-0.64903600	-2.35303100	-0.81087100
C	-1.37901000	-1.20526200	-0.45137800

C	-0.70684800	-0.03550500	-0.03593700
C	-1.41062900	1.13233800	0.32955100
C	-0.71177300	2.28194400	0.74127200
C	0.66383800	2.28336400	0.79265100
C	-2.83087700	-1.22623400	-0.50806300
N	-3.48511300	-0.03905300	-0.13791800
C	-2.86279000	1.14948700	0.27964300
C	-4.92186100	-0.03954900	-0.19205000
C	-5.57250300	0.26559800	-1.38034000
C	-6.95955700	0.25916100	-1.43341300
C	-7.72368000	-0.03979300	-0.29947800
C	-7.04720500	-0.36228500	0.88302100
C	-5.66072200	-0.35748700	0.94033300
C	-9.20975000	-0.00625100	-0.31967300
C	-9.95132700	-1.06036700	0.45140400
C	-11.11519300	-0.75529200	1.17110200
C	-12.30008100	0.19420900	-1.07892500
C	-11.30927000	1.18867600	-1.11662100
C	-9.85176100	0.89451900	-1.10537300
C	-12.11523900	-1.74898000	1.21344400
C	-13.57010700	-1.42013400	1.24448000
C	-14.18204500	-0.52422800	0.44414800
C	-13.47673900	0.50347400	-0.36977300
C	-9.62579100	-2.40210400	0.20105200
C	-10.48458000	-3.44416200	0.53906600
C	-11.76636800	-3.07529600	0.96234200
C	-13.82302800	1.84072200	-0.16569600
C	-12.96739800	2.88922200	-0.52044800
C	-11.67842700	2.52557400	-0.90499400
O	3.50632300	2.13128700	0.84748500
O	3.56529900	-2.19009600	-0.61217700
O	-3.54999600	2.12614900	0.57657800

O	-3.49179200	-2.20478900	-0.85420500
C	-13.41825000	4.34510600	-0.36387000
C	-13.75083800	4.63587600	1.11059600
C	-12.33987700	5.33617800	-0.81736800
C	-14.67536100	4.57581600	-1.22136500
C	-10.12453800	-4.92197100	0.35622700
C	-11.05036600	-5.56119100	-0.69421000
C	-8.67407200	-5.11001000	-0.10367400
C	-10.30225600	-5.65202400	1.69951700
C	9.99682300	4.91309300	0.37692000
C	8.72882400	5.28748600	-0.41114400
C	9.68008400	4.92843100	1.88309800
C	11.06554200	5.97692700	0.09989300
C	13.49671500	-4.27975400	-0.33859500
C	14.75522400	-4.62384300	0.47785700
C	12.43190000	-5.34449200	-0.05021900
C	13.83662200	-4.33191000	-1.83892100
C	11.31026700	-0.23757700	-1.97036200
C	12.13109300	0.89098900	1.89988200
C	-11.28020400	0.56795100	1.87134000
C	-12.13640600	-1.12873000	-1.77715200
H	14.19362600	2.40426300	-1.52930900
H	15.27480200	0.61013000	-0.46214700
H	9.26509400	-1.83689900	1.32515500
H	8.66869800	2.53358500	0.65686100
H	12.50154100	4.00376500	-0.49137900
H	14.80991000	-1.89000800	-0.66663500
H	10.97122900	-3.36704200	0.45638300
H	7.62130100	0.83385100	-1.71017600
H	5.14949900	0.80751600	-1.80039600
H	5.01676400	-0.83654200	2.14549400
H	7.48403000	-0.81132000	2.24707400

H	1.29846400	-3.22913200	-1.03828400
H	-1.19702400	-3.23358300	-1.12573500
H	-1.28346900	3.16096300	1.01564700
H	1.21170700	3.16340700	1.10914000
H	-4.98955700	0.49447100	-2.26648700
H	-7.45578300	0.47091100	-2.37460100
H	-7.61856200	-0.61306900	1.77086100
H	-5.14685500	-0.59962300	1.86487300
H	-9.22888500	1.61588200	-1.63031400
H	-14.20565300	-2.06408500	1.84987000
H	-15.26430300	-0.43812000	0.52308800
H	-8.68940500	-2.61048200	-0.30308900
H	-12.54140300	-3.83160200	1.05470400
H	-14.76449300	2.05443300	0.33342200
H	-10.90865500	3.28265500	-1.00913300
H	-14.07374700	5.67605600	1.22857500
H	-14.55555200	3.99402500	1.48070600
H	-12.87372100	4.47829800	1.74682000
H	-12.72308100	6.35817800	-0.73578900
H	-12.05033800	5.16960500	-1.85988500
H	-11.43970800	5.27210100	-0.19794700
H	-15.49346800	3.91294900	-0.92441800
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H	-12.10190400	-5.50647300	-0.39780700
H	-10.94619300	-5.06057800	-1.66244400
H	-8.44657700	-6.17837900	-0.17281200
H	-7.96527700	-4.66178600	0.59996200
H	-8.49881600	-4.67173400	-1.09123900
H	-11.33007000	-5.57757600	2.06686900
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H	-9.64034300	-5.23144700	2.46371500
H	8.37606500	6.28125900	-0.11442900
H	8.92849800	5.30539900	-1.48764900
H	7.91724900	4.57619800	-0.23156400
H	9.35345800	5.92754500	2.19163800
H	10.56529700	4.66390600	2.47082200
H	8.88279900	4.22452300	2.13869600
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H	10.67945800	6.96434500	0.37171000
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H	15.11906900	-5.62270000	0.21329800
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H	12.87086000	1.66370100	1.69135600
H	11.13686400	1.33170900	1.84395100
H	12.28306000	0.56356500	2.93609900
H	-11.23405600	0.38983000	2.95262000
H	-10.46939300	1.25151900	1.61730300
H	-12.22875100	1.06229200	1.66539800
H	-11.14664600	-1.56754000	-1.66059700
H	-12.88297800	-1.85102000	-1.44746800
H	-12.29350100	-0.96267200	-2.85038600

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