Supporting information for

Emission enhancement by intramolecular stacking between heteroleptic iridium(III) complex and flexibly bridged aromatic pendant group

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1. $^1$H NMR spectra of (trppy)$_2$Ir(pic)
**Figure S1.** Polarization optical microscope images showing a sample of MeCN grown crystals with the analyzer set at a several degree deviation to the both sides of the crossed configuration. The highlighted monocrystals show an opposite response to polarized light, indicating two different enantiopure forms.
2. Methodology of quantum chemical calculations

2.1. Statistical/computational analysis of conformers

Because TR groups are linked to the rigid aromatic core part of the (trppy)$_2$Ir(pic) complex by a flexible alkyl tether, their placement relatively to the core can vary greatly from one conformation to another, which can significantly affect optical properties of the whole complex due to the interaction of TR and core aromatic rings. Additionally, in ambient conditions the alkanes undergo active conformational changes and are most likely in thermodynamic equilibrium, which can also change with the exposure to different solvents. In order to identify the most probable geometries of (trppy)$_2$Ir(pic) a statistical/computational analysis of conformer distribution in geometry configuration–energy coordinates was performed. A set of conformers was chosen for the study, with 180 starting structures generated by “genetic” algorithm using MMFF94 force field in OpenBabel, using the criterion of lower energy to select the conformers. Next, all the conformers were subjected to a geometry optimization by HF-3c method, which is Hartree–Fock method but augmented by three corrections: the dispersion correction (crucial for describing non-covalent interactions, as is necessary for our problem), the basis-set superposition error correction (gCP by Grimme et al.) and the correction for limited basis set (MINIX in this method). These calculations were accomplished in ORCA, with 105 geometries converged for DCM and 100 for toluene (C-PCM model and SAS cavity). Subsequent energy calculations were done with these HF-3c-obtained geometries with the dispersion-corrected range-separated hybrid functional ωB97XD and larger basis set as described in the next section, which are the energies used in the analysis. These and all other calculations with DFT were performed using Gaussian 09, rev. D.01 software package.

Three different TR-to-complex binding modes were assessed: TR-to-Pic (either TR-to-COO or TR-to-pyridine contacts), TR-to-Ppy in edge-to-face fashion and TR-to-Ppy in face-to-face configuration. Edge-to-face contacts were defined as the closest (minimal) distances between any of H atoms on aromatic rings within Ppy (or Pic) ligands and the geometric center of any ring within a TR group. In a similar way, face-to-face contacts were defined as the distances between centroids of rings, of which one belongs to a ligand (Ppy or Pic) while another one – to a TR group. For COO, the center was assumed to be the C atom. These calculations and statistical analysis was carried out in Microsoft Excel using the Visual Basic for Applications module, as well as LibreOffice Calc. Data density plots were acquired with OriginPro 2018 using 2D Kernel Density tool and Bivariate Kernel Density Estimator method.
In the case of TR-to-Pic interaction the calculated distances between these aromatic systems are too large for any realistic interaction (the closest contact being 5.8–6.7 Å on average/median for 100 conformations). While this contradicts the TR-to-Pic oxygen conformation found in MeCN grown crystal it should be noted that with the specific starting geometries, aimed towards the convergence in TR-to-Pic fashion, such geometries, indeed, were obtained. This can be traced down to the insufficient solvent modelling by C-PCM in this case, as it does not account for non-electrostatic interactions with the solvent, such as the hydrogen bonds. As discussed in the main article, only the non-compatibility of extremely non-acidic C–H bonds in THF and repulsion between the carboxyl of Pic and the electronegative atoms in solvent molecules can make it feasible for the complex to systematically form such a weak hydrogen bond as the one present in the solid phase, shown on the Figure 1a. In all other solvents, interaction with their molecules will definitely be preferred. The C-PCM, however, is oblivious to such effects and tends to preferentially expose more polar parts of the molecule (the carboxyl group) to the polar solvent, as this maximizes the solvation energy for continuum solvation models to which C-PCM belongs. This leads to TR-to-Pic-bonded structures being largely misrepresented in the lowest-energy conformer statistics.

In contrast to TR-to-Pic, the distances between TR and Ppy, all, average, median and minimal (for all conformers), are much lower. In edge-to-face mode these parameters are around 3–3.5 Å. For face-to-face stacking configuration these parameters are around 4.5–5 Å, notably exceeding the value 3.8 Å that is generally considered as the upper limit for such aromatic interactions. Actually, this separation corresponds to the edge-to-face interaction, if we express it as the distance between the centroids of the interacting rings. This is also manifested by much more round shape (hence, greater randomness) of conformer distribution (Figure S2), describing various inclinations of the rings corresponding to much narrower span of H-to-centroid distances (Figure 4). It can be concluded that the TR and Ppy interaction proceeds strictly in edge-to-face fashion. Overall, there is larger energy advantage for smaller TR-to-Ppy edge-to-face and (to a lesser extent) face-to-face distances in more polar solvent. Together with the decrease in distance among the conformers (mean difference up to 0.08 Å), it can be concluded that in more polar solvents a larger portion of molecules will assume lower-energy conformations – those with closer TR-to-Ppy contacts.
Figure S2. Computational/statistical analysis of TR$_1$/TR$_2$ and Ppy binding tendency in face-to-face mode, showing the distribution of HF-3c-optimized conformations (dots) in toluene and DCM in relation to their ωB97XD energy and TR-Ppy distance.

2.2. Determination of the energy levels

For a selected conformer (with a maximal initial distance between TR groups), geometry optimization with more reliable DFT/basis set method was carried out in both toluene and DCM, for the lowest singlet (ground) and triplet states. As for basis set, it is commonly agreed that LANL2DZ for Ir atom (and 6-31G(d) otherwise) is adequate. We, however, chose D95V(d,p) as the basis for the lighter elements, as this is the basis set actually requested when LANL2DZ is used, which should have some justification of not using some native Pople-family basis set. Also, polarization functions on hydrogen atoms should be beneficial for describing non-covalent interactions of π systems, which frequently involve electrostatic interactions between electron-depleted hydrogen atoms and electron-rich π systems. Dispersion-corrected range-separated hybrid functional ωB97XD was used. To model solvent effects, simple but robust C-PCM model was employed (this time with 1.1-factor scaled van der Waals cavity). In the last stage of geometry optimizations, correct-within-the-method (not semi-empirical) force constants were employed and the first
frequencies were checked of being real to assure the structure corresponds to an energy minimum. SCF and geometry convergence criteria were left at their default values for Gaussian 09 (SCF: $10^{-8}$ for [F,P]; geometry: 4 criteria, on maximum and RMS force and coordinate change). The integration grid was left as “by default” for Gaussian 09 (“FineGrid”, or (75,302) pruned one).

Singlet and triplet levels were calculated using time-dependent density functional theory (TD-DFT) using ωB97XD functional and mixed basis set, with D95V(d,p) on light elements (C, N, O, H) and LANL2DZ on iridium atom – just as for the geometry optimization. For TR-to-Pic–stacked conformation the geometry obtained in single-crystal X-ray analysis was used. We checked if optimizing the triplet geometry (non-time-dependently) has any effect on the shape of singlet–triplet transition, and found it does have some (without taking the solvation effects on geometry in consideration), simultaneously intensifying the localization of the frontier NTOs and confining the transition overwhelmingly to the frontier pair of NTOs. Also, we checked the impact of optimizing the singlet geometry in solution – this time we observed a strong symmetrization of transitions in dichloromethane, although there are deviations of same character from the case of toluene even with the vacuum geometry. This triggered us to check if there is some impact of medium on the geometry of the triplet state, but we found no visible change (for DCM) or some minor but noticeable delocalization over the mirroring ligand (for toluene); so the overall locality of triplet state, at least as assessed without taking the spin–orbit coupling into account, seems to be confirmed. Also, it can be seen that the solvent effect on geometry is much stronger in the case of singlet – obviously because the triplet state is much more localized.

Natural transition orbitals (NTO)\textsuperscript{S14} were obtained by diagonalizing the transition density matrix in Gaussian, after the TD-DFT calculation. In all cases, it was possible to capture more than 90% of the transition in two frontier NTOs – except for triplet states with non-triplet geometries. The NTO difference plots, approximately showing the shift in electron density during the excitation or emission, were obtained in Multiwfn v. 3.4.1\textsuperscript{S15,16} and visualized in Avogadro v. 1.2.0.\textsuperscript{S17}

Ground-state molecular electrostatic potential (ESP) calculations for previously ωB97XD-optimized conformers of (trppy)$_2$Ir(pic) were performed using Multiwfn program and visualized with VMD software.\textsuperscript{S18}
Figure S3. PL spectra of (trppy)$_2$Ir(pic) in different polarity solvents.

Table S1

| Solvent | Dielectric constant ($\varepsilon$)$^a$ | pKa$^b$ | $\alpha$ | $\beta$ | SA$^c$ | SB$^c$ | $\lambda_{em,max}$, nm | $I_{PL}^d$ | FWHM,$^e$ cm$^{-1}$ | $\Delta$FWHM,$^f$ cm$^{-1}$ |
|---------|---------------------------------|--------|--------|--------|--------|--------|----------------------|--------|-----------------|-------------------|
| toluene | 2.38                            | 42$^g$ | 0.00   | 0.11   | 0.000  | 0.128  | 514                  | 0.48   | 2543            | 0                 |
| THF     | 7.58                            | >50$^h$| 0.00   | 0.55   | 0.000  | 0.591  | 516                  | 1.00   | 2570            | 27                |
| DCM     | 8.93                            | —      | 0.00   | 0.00   | 0.00   | 0.040  | 512                  | 0.51   | 2604            | 61                |
| MeCN    | 35.94                           | 25$^i$ | 0.19   | 0.31   | 0.044  | 0.286  | 513                  | 0.13   | 3561            | 1018              |
| DMSO    | 46.45                           | 35$^j$ | 0.00   | 0.76   | 0.072  | 0.647  | 516                  | 0.66   | 2606            | 63                |

$^a$ Values from reference S19

$^b$ Kamlet–Taft parameters characterizing hydrogen bond donating ($\alpha$) and hydrogen bond accepting ($\beta$) ability of solvents. S20

$^c$ Empirical parameters by Catalán and et al. characterizing solvent acidity (SA) and basicity (SB). S21

$^d$ Measured relative PL intensity in comparison to THF solution.

$^e$ Full width at half-maximum (FWHM) of PL bands.

$^f$ Relative PL band broadening in comparison to the value measured in toluene.

$^g$ See ref. S22.

$^h$ An estimation based on the value of benzyl methyl ether (pKa =49). S23

$^i$ See ref. S24.

$^j$ See ref. S25.
Figure S4. Lowest unoccupied and highest occupied molecular levels (LUMO and HOMO) of (trppy)$_2$Ir(pic). In vacuum LUMO+1 is mainly contained on Pic moiety, while LUMO resides on the pyridine ring of one of Ppy ligands. The increase of medium polarity reduces the energy gap between the two levels and the orbital configuration in LUMO and LUMO+1 becomes increasingly similar.
Figure S5. Photoluminescence spectra of (trppy)$_2$Ir(pic) in 2-methyltetrahydrofuran solution at room and 77K temperature.
3. Characterization of \((\text{trppy})_2\text{Ir(pic)}\) solid-state forms

3.1. DSC and TG analysis

Differential scanning calorimetry (DSC) and thermogravimetric (TG) plots are given in the Figure S6. They illustrate the thermal properties of a glassy sample, obtained by evaporation of DCM solution, and for precipitated material samples that were collected from MeCN, THF and 2-ethoxyethanol solutions. The first DSC scan of the DCM-cast sample reveals a signal characteristic for glass transition in amorphous compounds \(T_g\) at 124 °C, without any indications of presence of a crystalline phase. TGA curve shows 2% mass loss in the temperature range that is coincident with \(T_g\), and this process can be attributed to the release of trapped solvent inclusions. The second DSC curve, characterizing phase transitions of an initially melted sample, also displays a \(T_g\) peak, this time at 148 °C. The increased temperature and narrowed interval of this signal suggest that amorphous phase obtained from the melt have a more ordered molecular packing in comparison to the solution-cast glass.

The initial heating of the three other samples can be characterized by the presence of intensive endothermic DSC peaks that can be assigned to the melting process of a crystalline phase. MeCN- and THF-grown samples show additional endothermic signals, which coincide with a significant mass loss in TG curves, thus indicating that the crystalline structures are solvates. The scans of the melted crystalline samples reveal that the same amorphous phase forms in all cases, as the DSC curve for this sample is indistinguishable from that of previously observed one in the case of melted DCM-cast glass. This is an important observation, as it indicates that the described amorphous state is the most preferential solid phase packing arrangement of \((\text{trppy})_2\text{Ir(pic)}\) among the attainable solid-state packing configurations, and only in cases where the compound is exposed to polar solvents it assumes a crystalline form. It can be reasoned that the observed amorphous phase is composed of energetically-stabilized aggregated dimers, whose further packing into the even more energetically favorable crystalline state is obstructed by encapsulating TR groups.
Figure S6. DSC and TG thermograms of (trppy)$_2$Ir(pic) solid phase forms: glass cast from DCM solution (a). Crystalline forms acquired from MeCN (b), THF (c) and 2-ethoxyethanol (d) solutions. $T_g$ – glass transition temperature, $T_m$ – melting temperature, $T_{\text{desolv}}$ – desolvatation temperature.
Figure S7. PXRD patterns of different solid forms of (trppy)$_2$Ir(pic). DCM-cast (trppy)$_2$Ir(pic) glass features broad halos that are characteristic for amorphous compounds. Aggregates, on the other hand, show well-distinguishable reflection peaks, indicating the presence of the crystalline phase.
Figure S8. Comparison of (trppy)$_2$Ir(pic) PL bands in THF solution and 2-ethoxyethanol (EET)-grown crystals. The reduction in PL intensity, observed in the left shoulder of EET crystal band, is attributed to self-absorption due to the overlapping emission and absorption bands.
Figure S9. Scanning electron microscope (SEM) images of selected (trppy)$_2$Ir(pic) solid forms: glass cast from DCM (a) and aggregates formed in 1,4-dioxane (b), THF (c) and 2-ethoxyethanol (d). The amorphous DCM-cast glass exhibits irregular, massive lumps of the material with clearly visible voids. The spherical cavities are attributed to the expansion of residual solvent enclosures during thermal annealing. The precipitated crystalline solids obtained from polar solvents are composed of rod- or plate-like microstructures.
4. OLED characteristics

Table S2
Electroluminescence characteristics of (trppy)$_2$Ir(pic) based OLEDs.

| Host material, solvent $^a$ | $V_{on}^{b}$, V | $L_{max}$, cd·m$^{-2}$ | $\eta_{ext}^{c}$, % | $\eta_e^{d}$, cd·A$^{-1}$ | $\eta_P^{e}$, lm·W$^{-1}$ | $\lambda_{max}^{f}$, nm | CIE (x,y) |
|-----------------------------|-----------------|------------------------|---------------------|----------------------|----------------------|-------------------|------------|
| PVK, CHCl$_3$              | 9.0             | 7276                   | 2.5/1.8$^g$         | 3.6/2.6$^g$          | 1.4/1.3$^g$          | 518               | 0.37, 0.56 |
| CBP, CHCl$_3$              | 5.5             | 8751                   | 6.1/5.6             | 8.9/8.3              | 8.0/6.5              | 514               | 0.32, 0.59 |
| CBP, THF                   | 5.5             | 2363                   | 2.7/1.9             | 3.3/2.3              | 2.8/1.5              | 514               | 0.32, 0.59 |

$^a$Emitting layer was deposited by spin-coating, the concentration of the iridium (III) complex in the devices is 20 wt%. $^b$Voltage at which luminance of 1 cd m$^{-2}$ is measured. $^c$OLED’s external quantum efficiency. $^d$Current efficiency. $^e$Power efficiency. $^f$Measured at 11 V. $^g$Maximal achieved values and values measured at 1000 cd m$^{-2}$.

Figure S10. Electroluminescence (EL) spectra of OLED with PVK:(trppy)$_2$Ir(pic) (20 wt%) emitting layer at increasing driving voltage values. For comparison, photoluminescence (PL) spectra of (trppy)$_2$Ir(pic) are given in doped PVK (20 wt% complex content) and host-free amorphous films. The voltage-dependent transformation of EL spectra is interpreted as follows: initially the emission originates from non-aggregated complex molecules (EL@11V overlaps with host-dispersed complex emission) but with a gradual increase of voltage the emission starts to be dominated by the aggregates (EL@18V band can be interpreted as a combination of host-dispersed and host-free PL bands).
5. References

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6. Coordinates for DFT-optimized structures used for energy level determination

ωB97XD /[D95V(d,p) (C, N, O, H), LANL2DZ (Ir)] (vacuum) non-stacked conformation

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Ir   | -0.075645061 | 2.921030236 | 0.200670555 |
| N    | -0.307224510 | 3.072000674 | -1.826259067 |
| N    | 0.080956432 | 2.602547486 | 2.228521889 |
| C    | -1.488000777 | 1.519595691 | 0.427853446 |
| N    | 1.314785416 | 4.587150604 | 0.121133193 |
| O    | -1.335955528 | 4.644354744 | 0.610304011 |
| C    | 1.211281421 | 1.516316512 | -0.379193946 |
| C    | -2.304815659 | 0.951358959 | -0.556997917 |
| C    | -3.287212166 | 0.008989284 | -0.243638672 |
| C    | -3.463613794 | -0.408021519 | 1.081323336 |
| C    | -2.654586427 | 0.125615331 | 2.077628108 |
| C    | -1.678471275 | 1.078726843 | 1.758750454 |
| C    | -0.789846115 | 1.693914657 | 2.745141360 |
| C    | -0.779136329 | 1.418250115 | 4.119427667 |
| C    | 0.115811952 | 2.072475006 | 4.952831081 |
| C    | 0.945124055 | 3.237707439 | 3.038126614 |
| C    | 1.001698983 | 3.005228919 | 4.402736212 |
| H    | -1.475948448 | 0.692707264 | 4.522580163 |
| H    | 0.126865669 | 1.863482887 | 6.018377410 |
| H    | 1.716165036 | 3.545728280 | 5.017769094 |
| H    | 1.609169053 | 3.950197645 | 2.561955786 |
| H    | -4.231070779 | -1.134832274 | 1.324081409 |
| H    | -2.802969066 | -0.205251763 | 3.102575212 |
| H    | -2.183956883 | 1.249481456 | -1.597751483 |
| C    | 0.467706434 | 2.243382832 | -2.575006069 |
| C    | -1.186001528 | 3.904115615 | -2.409452110 |
| C    | -1.335107579 | 3.963219168 | -3.787247476 |
| C    | 0.360397835 | 2.264434567 | -3.970571694 |
| C    | -0.542562967 | 3.172254917 | -4.580156839 |
| H    | -2.057607517 | 4.645601205 | -4.219902038 |
| H    | -0.636075022 | 3.145651812 | -5.661950285 |
| H    | 0.976164778 | 1.602086767 | -4.568228845 |
| H    | -1.776827752 | 4.511294517 | -1.730111275 |
| C    | 1.348740524 | 1.378577703 | -1.781997332 |
| C    | 2.038644784 | 0.716334558 | 0.427519571 |
| C    | 2.270775142 | 0.480239275 | -2.341233484 |
| C    | 3.074746305 | -0.293783191 | -1.515920656 |
| C    | 2.963039162 | -0.171353155 | -0.120984048 |
| H    | 1.962310532 | 0.795476524 | 1.510884566 |
| H    | 2.569963110 | 0.381222022 | -3.419448232 |
| H    | 3.797166416 | -0.988470864 | -1.934471231 |
| C    | 3.832465465 | -1.013312788 | 0.773625176 |
| O    | 5.203568829 | -0.787041909 | 0.397633939 |
| H    | 3.624037438 | -2.081744459 | 0.647747704 |
| H    | 3.692051060 | -0.758157589 | 1.827180211 |
| C    | 6.128634612 | -1.362888725 | 1.176571605 |
| Atoms | x       | y       | z       |
|-------|---------|---------|---------|
| O     | 5.865428463 | -1.932514927 | 2.214960965 |
| C     | 7.516109841  | -1.180006505 | 0.586952250 |
| C     | 8.116513925  | -2.475302498 | -0.056007431 |
| H     | 8.167115388  | -0.804287272 | 1.379322471 |
| C     | 4.473223831  | -0.416989358 | -0.189968135 |
| C     | 8.751876251  | -3.429494339 | 0.975471879 |
| C     | 6.958523130  | -3.160405110 | -0.802112517 |
| C     | 9.260391033  | -2.045985880 | -0.998321810 |
| O     | 9.472912744  | -4.539759416 | 0.505626854 |
| C     | 10.075956311 | -5.435167248 | 1.384003589 |
| C     | 9.976698428  | -5.239552903 | 2.765700340 |
| C     | 9.258870442  | -4.145805979 | 3.244308475 |
| C     | 8.647556100  | -3.252299988 | 2.35708261 |
| C     | 6.316862059  | -4.281825296 | -0.267945728 |
| C     | 5.192014524  | -4.831015240 | -0.889992729 |
| C     | 4.688583908  | -8.266595977 | -2.061459727 |
| C     | 5.316409078  | -3.138497854 | -2.599404686 |
| C     | 6.430207169  | -2.587581956 | -1.969352077 |
| C     | 9.482437035  | -2.659489334 | -2.237419338 |
| C     | 10.575426184 | -3.106517663 | -3.032125311 |
| C     | 10.183545771 | -1.080900243 | -0.571063195 |
| C     | 11.276015057 | -0.723464565 | -1.360961499 |
| C     | 11.477058913 | -1.333128181 | -2.600918540 |
| H     | 9.568305622  | -3.107693037 | -0.563220566 |
| H     | 10.626986940 | -6.224842761 | 0.990656446 |
| H     | 10.448847251 | -5.933745245 | 3.455209432 |
| H     | 9.157350486  | -3.985549464 | 4.314037537 |
| H     | 8.054484667  | -2.443409435 | 2.766649806 |
| H     | 3.816479465  | -4.693992921 | -2.547912274 |
| H     | 4.934203343  | -2.685324211 | -3.510465777 |
| H     | 6.887732548  | -4.728463811 | 0.648742933 |
| H     | 4.710689705  | -5.701066221 | -0.452606045 |
| H     | 6.891740639  | -1.697665090 | -2.389523215 |
| H     | 8.797576316  | -4.235517477 | -2.592279351 |
| H     | 10.069255762 | -0.609426524 | 0.406082499 |
| H     | 11.975909067 | 0.026318302 | -1.001891905 |
| H     | 10.721033855 | -2.798305544 | -3.989924521 |
| C     | 12.327262387 | -1.057569527 | -3.218364386 |
| C     | -5.943229001 | -2.023343883 | -1.631780623 |
| O     | -6.678235827 | -3.160036786 | -0.954930059 |
| O     | -6.267930838 | -1.495003734 | -2.673101640 |
| C     | -7.979012561 | -2.714178485 | -0.221412816 |
| H     | -6.005457018 | -3.604177209 | -0.218439735 |
| H     | -6.990043117 | -3.906647257 | -1.719809814 |
| C     | -9.047028830 | -2.178943849 | -1.198709280 |
| C     | -8.623121129 | -3.934119266 | 0.473466055 |
| C     | -7.540412836 | -1.667100802 | 0.815985354 |
| C     | -9.217883601 | -2.754748224 | -2.463448250 |
| C     | -10.255793494 | -2.357325145 | -3.305564144 |
| C     | -11.157259797 | -1.371802931 | -2.899082355 |
ωB97XD /D95V(d,p) (C, N, O, H), LANL2DZ (Ir), C-PCM (toluene) non-stacked conformation

Ir  0.000387357  3.009568300  0.204304961
N  -0.196562444  3.157616494 -1.830208809
N   0.138442769  2.694460589  2.235605763
C  -1.480125577  1.679712709  0.437050498
H   3.451962872  7.809045846  0.054354221
H   3.026290756  3.524251133 -0.334564392
H  -3.609779196 -0.705005460 -2.25791014
H  -4.927425709  0.277537376 -1.607057133

C  -11.00434937  -0.793048981 -1.638798291
C  -9.963394859  -1.195868853 -0.801399901
H  -8.538463406  -3.523569798 -2.815602491
H  -10.358262160 -2.819286633 -4.28449156
H  -11.964219753 -1.059219989 -3.555755438
H  -11.696021875 -0.026207507 -1.301866633
H  -9.867345749  -0.726242190  0.172857532
C  -8.115887696  -5.232487736  0.369154309
C  -9.783042520  -3.746069199  1.235984780
C  -10.419287409 -4.811948301  1.868333434
C  -9.903477336  -6.107525308  1.751418814
C  -8.749315033  -6.310152515  0.999178517
H  -8.331576586  -7.307948286  0.897198721
H  -10.396411289 -6.943392947  2.236268270
H  -7.216593560  -5.435879150 -0.201431435
H  -10.206493490 -2.749695861  1.338706985
H  -11.319472733  -4.633427943  2.449738363
C  -7.320585515  -0.328951842  0.436305417
C  -7.226822186  -2.028540981  2.128836193
C  -6.826062497  0.608268430  1.337483940
C  -6.537007680   0.234688998  2.652604584
C  -6.736161474  -1.089666477  3.041449181
H  -7.538991889  -0.018533479 -0.585107686
H  -6.655386112  1.630514963  1.012710436
H  -6.150008239  0.965497559  3.356784787
H  -7.372308940  -3.054834551  2.452986596
H  -6.510785307  -1.399505297  4.058293777
C  -4.183568548  -0.485334383 -1.350696986
O  -4.864382437  -1.664411110 -0.920459120
C   0.744417317   5.781047764  0.397499027
C   1.484167603   6.961349941  0.342824226
C   2.849218777   6.897475549  0.072170291
C   2.627383129   4.517597420 -0.147390000
C   3.432012016   5.651747166 -0.178595381
C  -0.767497869   5.796468147  0.638036769
O  -1.293606187   6.885755966  0.840881281
H   0.962091076   7.890783421  0.542068886
H   4.490061004   5.552523468 -0.395634317
H   3.451962872   7.809045846  0.054354221
H   3.026290756   3.524251133 -0.334564392
H  -3.609779196  -0.705005460 -2.25791014
H  -4.927425709   0.277537376 -1.607057133
| Atom  | x         | y         | z          |
|-------|-----------|-----------|------------|
| C     | 9.036510956 | -6.266722251 | 2.158816492 |
| C     | 8.658341791  | -5.130532574 | 2.873000982 |
| C     | 8.269106206  | -3.966478233 | 2.201871089 |
| C     | 5.969789413  | -3.896866717 | 1.034585354 |
| C     | 4.987441024  | -4.046865454 | 2.017192637 |
| C     | 4.938948285  | -3.173529012 | 3.051444849 |
| C     | 5.869871223  | -2.133389107 | 3.186838741 |
| C     | 6.842135250  | -1.983189845 | 2.198710557 |
| C     | 9.813565465  | -2.607273160 | 1.730496860 |
| C     | 10.110537340 | -2.245918697 | 2.163432368 |
| C     | 11.101830765 | -0.929416635 | 0.170495370 |
| C     | 10.886641521 | -1.402364579 | 0.138530085 |
| H     | 8.634788849  | -5.055239981 | 0.987673177 |
| H     | 9.310147347  | -7.100862126 | 0.185071071 |
| H     | 9.336081637  | -7.171369543 | 2.680083647 |
| H     | 8.656841732  | -5.145334847 | 3.959273339 |
| H     | 7.957327089  | -3.115406718 | 2.795375944 |
| H     | 4.179248768  | 3.292761590  | 3.872413749 |
| H     | 8.348165641  | -1.432423127 | 4.016017315 |
| H     | 5.85872856  | -4.584056976 | -0.194284793 |
| H     | 4.258963907  | -4.847670776 | -1.928715021 |
| H     | 7.549740114  | -1.161959524 | -2.273682733 |
| H     | 9.212948017  | -3.258659354 | -2.358117440 |
| H     | 9.764573918  | -0.921086470 | 1.216095584 |
| H     | 10.995467775 | -0.277391764 | 0.451130467 |
| H     | 11.461096757 | -2.627495023 | -3.110087741 |
| H     | 12.880705958 | -1.120936989 | -1.720597420 |
| C     | -5.987941516 | -1.96003016 | -1.626971608 |
| C     | -6.624490363 | -3.021718717 | -1.008656743 |
| O     | -6.394223857 | -1.211562398 | -2.610371366 |
| C     | -7.935873397 | -2.712308250 | -0.226538225 |
| C     | -5.906454622 | -3.461579626 | -0.313878006 |
| C     | -6.306195595 | -3.734772270 | -1.814597318 |
| C     | -9.070015867 | -2.229593330 | -1.155763012 |
| C     | -8.467740083 | -4.007738135 | 0.424746376 |
| C     | -7.552112415 | -1.675925700 | 0.848378883 |
| C     | -9.241302869 | -2.795893919 | -2.426038790 |
| C     | -10.329821582 | -2.456678586 | -3.229811717 |
| C     | -11.283516197 | -1.541097840 | -2.777832560 |
| C     | -11.328191111 | -0.977831184 | -1.509694653 |
| C     | -10.041692137 | -1.323472009 | -0.710286945 |
| C     | -8.526778738 | -3.517416266 | -2.808631914 |
| C     | -10.432721315 | -2.910581790 | -4.211376722 |
| C     | -12.130046651 | -1.273165953 | -3.403554769 |
| C     | -11.865570160 | -0.267768096 | -1.136750726 |
| C     | -9.954782552 | -0.871663802 | 0.272816359 |
| C     | -7.891117199 | -5.263926945 | 0.215346738 |
| C     | -9.602823430 | -3.935489216 | 1.249318067 |
| C     | -10.140313419 | -5.073809350 | 1.842546354 |
### ωB97XD /[D95V(d,p) (C, N, O, H), LANL2DZ (Ir)] C-PCM (DCM) non-stacked conformation

| Atom | ωB97XD | D95V(d,p) | LANL2DZ (Ir) | C-PCM (DCM) |
|------|--------|----------|--------------|-------------|
| C    | 0.092465280 | 3.464403622 | 0.143563235 | 0.143563235 |
| N    | -0.092105392 | 3.503284455 | -1.900316269 | -1.900316269 |
| O    | 3.266955277 | 2.190780386 | 2.190780386 | 2.190780386 |
| C    | 2.240468092 | 4.60034809 | 4.60034809 | 4.60034809 |
| N    | 4.960590556 | 0.500869920 | 0.500869920 | 0.500869920 |
| O    | 5.358905556 | 0.459347697 | 0.459347697 | 0.459347697 |
| C    | 1.875536988 | -0.313682421 | -0.313682421 | -0.313682421 |
| C    | 1.687560604 | -0.491957285 | -0.491957285 | -0.491957285 |
| C    | 0.859548649 | -0.120270898 | -0.120270898 | -0.120270898 |
| C    | 1.076136102 | 2.197050030 | 2.197050030 | 2.197050030 |
| C    | 1.909369495 | 1.816289955 | 1.816289955 | 1.816289955 |
| C    | 2.489466207 | 2.766518459 | 2.766518459 | 2.766518459 |
| C    | 2.293870062 | 4.152181960 | 4.152181960 | 4.152181960 |
| C    | 3.849323671 | 2.957033307 | 2.957033307 | 2.957033307 |
|  |  |  |  |
|---|---|---|---|
| C | 1.204424665 | 3.690188229 | 4.333632939 |
| H | -1.506519875 | 1.672037718 | 4.604058156 |
| H | 0.229750255 | 2.745545905 | 6.017442724 |
| H | 1.983914415 | 4.178682146 | 4.906305954 |
| H | 1.897694370 | 4.452807751 | 2.440201070 |
| H | -4.433726101 | -0.090061199 | 1.520790230 |
| H | -2.926879047 | 0.829851994 | 3.241378881 |
| H | -2.184962447 | 1.899752925 | -1.549162396 |
| C | 0.596900157 | 2.544009872 | -2.572667625 |
| C | -0.840578782 | 4.397766089 | -2.567747319 |
| C | -0.942461257 | 4.386186965 | -3.951010287 |
| C | 0.534681566 | 2.486581615 | -3.968945130 |
| C | -0.237739999 | 3.410886154 | -4.663085751 |
| H | 1.082279374 | 1.719980193 | -4.504573452 |
| H | -1.368131552 | 5.121440436 | -1.955407346 |
| C | 1.346048176 | 1.629445464 | -1.700497548 |
| C | 1.882543057 | 1.018804711 | 0.568103485 |
| C | 2.151727036 | 0.583411794 | -2.176379589 |
| C | 2.816649637 | -0.243390428 | -1.279344262 |
| C | 2.680382945 | -0.026414769 | 0.101589916 |
| O | 1.793932126 | 1.173885385 | 1.641909784 |
| H | 2.266488589 | 0.405432178 | -3.24214134 |
| C | 3.443869418 | -1.054126335 | -1.640185672 |
| C | 3.372932202 | -0.948742437 | 1.069207415 |
| O | 4.773474199 | -0.964541897 | 0.736229791 |
| H | 2.987265336 | -1.970339934 | 0.985261250 |
| C | 3.247778915 | -0.614776881 | 2.102893009 |
| C | 5.526920973 | -1.864334089 | 1.377698897 |
| O | 5.104366616 | -2.580118483 | 2.264982784 |
| C | 6.949268190 | -1.852785383 | 0.861681058 |
| C | 7.323592353 | -3.124001144 | 0.044603409 |
| H | 7.601821686 | -1.727025288 | 1.726860857 |
| H | 7.071015417 | -0.981621823 | 0.215621311 |
| C | 7.421120938 | -4.390442757 | 0.922183391 |
| C | 6.252060760 | -3.236392539 | -1.057482197 |
| C | 8.733506074 | -2.951468797 | -0.562646593 |
| C | 7.211321897 | -5.663001972 | 0.370748250 |
| C | 7.420910801 | -6.822170980 | 1.118874283 |
| C | 7.854163244 | -6.736683233 | 2.444409458 |
| C | 8.074166409 | -5.476293104 | 3.004699038 |
| C | 7.862141543 | -4.320647845 | 2.249736012 |
| C | 5.033863585 | -3.889754962 | -0.819427573 |
| C | 4.023335333 | -3.903641149 | -1.781586542 |
| C | 4.205214231 | -3.253650787 | -3.005307258 |
| C | 5.402107111 | -2.573591219 | -3.242549770 |
| C | 6.409776618 | -2.561995045 | -2.274917129 |
| C | 9.177621520 | -3.859355115 | -1.538378721 |
| C | 10.459120116 | -3.774097071 | -2.076425129 |
| Atoms | x         | y         | z         |
|-------|-----------|-----------|-----------|
| C     | 9.622986830 | -1.958752598 | -0.139093529 |
| C     | 10.913990348 | -1.869788235 | -0.673801179 |
| C     | 11.340057569 | -2.774990163 | -1.644660141 |
| H     | 6.874600486  | -5.762225670 | -0.656571819 |
| H     | 7.247830999  | -7.92257020  | 0.661786670 |
| H     | 8.018847490  | -7.637018323 | 3.029167035 |
| H     | 8.413453641  | -5.388059042 | 4.032899937 |
| H     | 8.504244444  | -3.362039020 | 2.721074156 |
| H     | 3.421754190  | -3.266715596 | -3.757288598 |
| H     | 5.554574877  | -2.050228463 | -4.182059440 |
| H     | 4.867354799  | -4.397245966 | 0.125977909 |
| H     | 3.091358417  | -4.420626117 | -1.572193529 |
| H     | 7.330978927  | -2.024304366 | -2.479037632 |
| H     | 8.509689816  | -4.639783431 | -1.891778126 |
| H     | 9.333759236  | -1.231902738 | 0.611845298 |
| H     | 11.583506092 | -1.088044215 | -0.326532945 |
| H     | 10.772297742 | -4.488153267 | -2.832628139 |
| H     | 12.339935018 | -2.704642197 | -0.062878662 |
| C     | -5.690297940 | -1.569525226 | -1.51676918 |
| C     | -6.024203439 | -2.944915122 | -0.982732677 |
| O     | -7.375216822 | -2.993224258 | -0.209897584 |
| H     | -5.228904963 | -3.250430659 | -0.300573893 |
| H     | -6.023584567 | -3.629044455 | -1.832550174 |
| C     | -8.596618927 | -2.797808477 | -1.133426265 |
| C     | -7.566840265 | -4.394063534 | -0.411973130 |
| C     | -7.262762598 | -1.912823823 | 0.884129847 |
| C     | -8.591225222 | -3.275022759 | -2.450536442 |
| C     | -9.735393550 | -3.216135909 | -3.248611930 |
| C     | -10.922116500 | -2.678938159 | -2.743972344 |
| C     | -10.945083904 | -2.206116434 | -1.429647910 |
| C     | -9.797526632 | -2.269330642 | -0.637560544 |
| C     | -7.692648081 | -3.705438155 | -2.879535955 |
| C     | -9.696697728 | -3.593249299 | -4.66648863 |
| C     | -11.813322161 | -2.631627321 | -3.363060035 |
| C     | -11.857725530 | -1.787403740 | -1.015152023 |
| C     | -9.849231271 | -1.894444727 | 0.379874398 |
| C     | -6.792442596 | -5.499585529 | 0.045390053 |
| C     | -8.594694362 | -4.593372744 | 1.348852360 |
| C     | -8.834080867 | -5.847080512 | 1.905157235 |
| C     | -8.050285857 | -6.945692063 | 1.531555933 |
| C     | -7.030752226 | -6.763885176 | 0.598257534 |
| C     | -6.411842655 | -7.603750748 | 0.295547675 |
| C     | -8.232867407 | -7.924819202 | 1.964577935 |
| C     | -5.987616124 | -5.404626735 | -0.675234387 |
| C     | -9.213039777 | -3.755262061 | 1.657648124 |
| C     | -9.631421333 | -5.967916761 | 2.632912549 |
| C     | -7.591111720 | -0.574971677 | 0.619613027 |
| C     | -6.690716663 | -2.215225538 | 2.126514592 |
| C     | -7.394034153 | 0.419154235 | 1.578959557 |
X-ray analysis-based structure used to determine molecular orbitals in vacuum, toluene and DCM
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -0.807185999 | -1.063925999 | -2.132223970 |
| C    | -2.771753091  | 0.149793877  | -2.042506196  |
| C    | -3.369574555  | -0.591147117  | -3.043866246  |
| C    | -1.339946746  | 1.825256778  | -3.166028898  |
| C    | -2.617318235  | -1.605892107  | -3.613824952  |
| H    | -4.256876271  | -0.375093616  | -3.311567401  |
| H    | -2.977083198  | -2.138833835  | -4.325006011  |
| C    | -0.816649900  | 2.522602678   | -3.569831812  |
| H    | -3.337399140  | 0.828997627   | -1.666601459  |
| C    | 0.473887099   | -2.865652245  | -1.430276742  |
| C    | 1.915465894   | -0.620114639  | 0.555318780   |
| C    | 1.369581657   | -2.283650924  | -1.823475070  |
| C    | 2.528980857   | -2.438221725  | -1.102031238  |
| C    | 2.823960602   | -1.624713635  | -0.023208280  |
| H    | 2.120882093   | -0.071551649  | 1.115132486   |
| H    | 1.166681769   | -2.842311500  | -2.576531052  |
| C    | 3.166593425   | -3.111422299  | -1.34782057   |
| C    | 4.100742154   | -1.823161189  | 0.768824427   |
| O    | 5.120118990   | -0.915974268  | 0.213384948   |
| H    | 4.398127469   | -2.743927427  | 0.697132753   |
| H    | 3.948260639   | -1.621548732  | 1.705948926   |
| C    | 6.299889123   | -1.463126769  | -0.036922405  |
| O    | 6.541598504   | -2.614600302  | 0.171224223   |
| C    | 7.206123471   | -0.431299785  | -0.656065910  |
| C    | 8.69866953    | -0.540237757  | -0.154471688  |
| H    | 8.366749083   | 0.451912573   | -0.447488860  |
| H    | 7.189948216   | -0.534425073  | -1.620715098  |
| C    | 8.633181953   | -0.236624643  | 1.365662739   |
| C    | 9.345237461   | -1.883939186  | -0.508425952  |
| C    | 9.545614501   | 0.573672991   | -0.835851689  |
| C    | 8.598208205   | 1.074849403   | 1.818210037   |
| C    | 8.485994158   | 1.341799809   | 3.159217519   |
| C    | 8.402193755   | 0.333174963   | 4.105110988   |
| C    | 8.404118584   | -0.952147836  | 3.673148405   |
| C    | 8.495077698   | -1.245370077  | 2.309459004   |
| C    | 10.367903928  | -2.433347638  | 0.244805755   |
| C    | 10.980537827  | -3.606573040  | -0.102020517  |
| C    | 10.580206454  | -4.315561086  | -1.238376666  |
| C    | 9.577565430   | -3.794055583  | -2.018211732  |
| C    | 8.977899496   | -2.584215944  | -1.663514334  |
| C    | 10.845077183  | 0.840011111   | -0.339326386  |
| C    | 11.648355017  | 1.804052032   | -0.879597973  |
| C    | 9.112698616   | 1.344031471   | -1.912371556  |
| C    | 9.928584786   | 2.339261862   | -2.457678055  |
| C    | 11.177190041  | 2.575366751   | -1.956901801  |
| H    | 8.646524758   | 1.797972685   | 1.190529269   |
| H    | 8.444363149   | 2.260113644   | 3.435960329   |
| H    | 8.385147210   | 0.529140861   | 5.043562420   |
| H    | 8.311450017   | -1.657786885  | 4.316762832   |
| H    | 8.458341102   | -2.158868394  | 2.019031449   |
O   -5.243885373  -2.624475220   2.023734924
C   -0.720484847   3.518132497  -1.502231004
C   -0.357065334   4.591014471  -2.315213839
C    0.823398953   4.530311411  -3.026247236
C    1.208220569   2.368947306  -2.082455871
C    1.609502022   3.408518562  -2.907527135
C   -2.010230469   3.516401653  -0.684014528
O   -2.751168186   4.483182346  -0.751075097
H   -0.932828527   5.358048448  -2.362192263
H    2.430271488   3.341027693  -3.401534391
H    1.103343946   5.253374415  -3.592620534
H    1.756495455   1.587366744  -1.996990555
H   -3.793121084  -3.901817462   2.557208817
H   -3.767056194  -3.548247127   1.027685459