An S-Shaped Double Helicene Showing both Multi-Resonance Thermally Activated Delayed Fluorescence and Circularly Polarized Luminescence

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Figure S1. Chemical structures of prior examples of N-Carbonyl MR-TADF emitters.[1–11]

1. Experimental Section

General Synthetic Procedures. All reagents and solvents were obtained from commercial sources and used as received. Air-sensitive reactions were performed under a nitrogen atmosphere using Schlenk techniques, no special precautions were taken to exclude air or moisture during work-up. DCM was obtained from a MBraun SPS5 solvent purification system. Flash column chromatography was carried out using silica gel (Silia-P from Silicycle,
60 Å, 40-63 µm). Analytical thin-layer-chromatography (TLC) was performed with silica plates with aluminum backings (250 µm with F-254 indicator). TLC visualization was accomplished by 254/365 nm UV lamp. HPLC analysis was conducted on a Shimadzu LC-40 HPLC equipped with a Shim-pack GIST 3µm C18 reverse phase analytical column. GCMS analysis was conducted using a Shimadzu QP2010SE GC-MS equipped with a Shimadzu SH-Rtx-1 column (30 m × 0.25 mm). ¹H and ¹³C NMR spectra were recorded on a Bruker Advance spectrometer (400 MHz for ¹H and either 101 or 126 MHz for ¹³C). The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet, and “dd” for doublet of doublets. ¹H and ¹³C NMR spectra were referenced residual solvent peaks with respect to TMS (δ = 0 ppm). Melting points were measured using open-ended capillaries on an Electrothermal 1101D Mel-Temp apparatus and are uncorrected. High-resolution mass spectrometry (HRMS) was performed in the School of Chemistry of the University of Leeds.

2. Synthetic procedures and characterization data

**Tetramethyl 2,2',2'',2'''-(1,3-phenylenebis(azanetriyl))tetrabenzoate (1):**

A 2-neck flask held under nitrogen was charged with benzene-1,3-diamine (2.66 g, 24.6 mmol, 1 equiv.), methyl 2-iodobenzoate (38.7 g, 21.7 mL, 148 mmol, 6 equiv.), copper (929 mg, 14.8 mmol, 0.6 equiv.), copper(I) iodide (656 mg, 3.44 mmol. 0.14 equiv.), anhydrous potassium carbonate (20.4 g, 148 mmol, 6 equiv.), and 50 mL anhydrous di-n-butyl ether. The resulting reaction mixture was heated to reflux and stirred for 48 hours. After cooling to room temperature, the mixture was filtered through a pad of celite. The filtrate was then mixed with dichloromethane (50 mL) and washed with water (3 × 50 mL). The organic layer was then dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting
dark brown oil was purified by column chromatography on silica gel (EtOAc : hexane = 20 : 80). The corresponding fractions were collected and evaporated under reduced pressure to afford the desired product as a brown reddish solid (8.80 g, 55%). Rₖ: 0.10 (EtOAc : hexane = 20 : 80). Mp: 170–172 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.46 (m, 8H), 7.13 (t, $J = 7.5$ Hz, 4H), 7.07–6.99 (m, 5H), 6.31 (dd, $J = 8.1, 2.2$ Hz, 2H), 6.15 (t, $J = 2.2$ Hz, 1H), 3.38 (s, 12H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 167, 149, 145, 132, 130, 129, 128, 127, 124, 115, 115, 52. HR-MS [M+H]$^+$ Calculated: 645.2237 (C$_{38}$H$_{33}$N$_2$O$_8$); Found: 645.2221.

**Diacridino[10,4-ab:10',4'-ij][1,7]phenanthroline-6,10,18,22-tetraone (Hel-DiDiKTa):**

![Image of molecular structure of Diacridino[10,4-ab:10',4'-ij][1,7]phenanthroline-6,10,18,22-tetraone (Hel-DiDiKTa)](image)

Compound 1 (5.0 g, 7.8 mmol, 1 equiv.) was combined with sodium hydroxide (3.1 g, 78 mmol, 10 equiv.) in 100 mL of an ethanol/water (1:1) mixture. The reaction was heated to reflux for 12 h. After cooling to room temperature, the pH was adjusted to 2-3 by addition of dilute hydrochloric acid. The tetra-acid precipitated as a brown greenish solid and was collected by vacuum filtration, washed thoroughly with water, dried under vacuum (4.52 g, 99% yield) and used without further purification and characterization. The tetra-acid (2.5 g, 4.25 mmol, 1 equiv.) was dispersed in 60 mL dichloromethane under a nitrogen atmosphere. To the reaction mixture were added sequentially thionyl chloride (20.2 g, 12.3 mL, 170 mmol, 40 equiv.) and 6 drops of N,N-dimethylformamide. After 3 h under reflux, the reaction mixture was cooled to room temperature. Under a positive flow of nitrogen, aluminium chloride (11.3 g, 85.0 mmol, 20 equiv.) was added slowly with stirring (exothermic reaction). After refluxing for 24 h, the reaction mixture was cooled to room temperature, and the reaction quenched by slow dropwise of water under vigorous stirring (exothermic reaction). The resulting mixture was combined with more dichloromethane (50 mL), the organic layer separated and washed with water (3 × 50 mL), and then dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the brown solid crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$:EtOAc = 7:3) to yield (rac)-Hel-DiDiKTa as an orange solid (0.79 g,
36\%). Rf: 0.60 (CH$_2$Cl$_2$:EtOAc = 7:3). Mp: > 390 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.71–8.50 (m, 5H), 8.37 (d, $J = 7.9$ Hz, 2H), 8.26 (m, 3H), 7.94 (t, $J = 7.7$ Hz, 1H), 7.81 (t, $J = 7.6$ Hz, 1H), 7.67 (t, $J = 7.4$ Hz, 2H), 7.46–8.50 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 179, 176, 139, 139, 133, 132, 130, 127, 126, 125, 123, 123, 122. Anal. Found: C, 78.18%; H, 3.14%; N, 5.21. Anal. Calcd. For C$_{34}$H$_{17}$N$_2$O$_4$: C, 79.06%; H, 3.12%; N, 5.42%. HR-MS [M+H]$^+$ Calculated: 517.1188 (C$_{34}$H$_{17}$N$_2$O$_4$); Found: 517.1177. 99.1% pure on HPLC analysis, retention time 31.3 minutes in 60% methanol 40% water.

Figure S2. $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 1.
Figure S3. DEPTq (101 MHz, DMSO-$d_6$) of compound 1.

Figure S4. $^1$H NMR (400 MHz, DMSO-$d_6$) of (rac)-Hel-DiDiKTa.
Figure S5. DEPTq (126 MHz, DMSO-$d_6$) of (rac)-Hel-DiDiKTa.

Figure S6. HRMS of (rac)-Hel-DiDiKTa.
Figure S7. HPLC trace of \((rac)\)-Hel-DiDiKTa.

3. X-Ray Crystallography

X-ray diffraction data for \((rac)\)-Hel-DiDiKTa were collected at 173 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P100 diffractometer \([\text{Cu K}_{\alpha} \text{ radiation (} \lambda = 1.54187 \text{ Å)}\)]. Intensity data were collected using both \(\omega\) and \(\varphi\) steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Data for all compounds analysed were collected using CrystalClear\(^{[12]}\) and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro,\(^{[13]}\) The structure was solved by dual-space methods (SHELXT\(^{[14]}\)) and refined by full-matrix least-squares against \(F^2\) (SHELXL-2018/3\(^{[15]}\)). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the Olex2\(^{[16]}\) interface. Deposition number 2105660 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data
Crystal data for (rac)-Hel-DiDiKTa. $\text{C}_{34}\text{H}_{16}\text{N}_{2}\text{O}_{4}$, $M = 516.49$, orthorhombic, $a = 14.2194(2)$, $b = 14.4571(2)$, $c = 21.6864(3)$ Å, $U = 4458.10(11)$ Å$^3$, $T = 173$ K, space group $\text{Pbca}$ (no. 61), $Z = 8$, 45132 reflections measured, 4079 unique ($R_{\text{int}} = 0.0281$), which were used in all calculations. The final $R_1 [I > 2\sigma(I)]$ was 0.0399 and $wR_2$ (all data) was 0.0974.
4. Photophysical data

Figure S8. (a) Absorption spectrum of (rac)-Hel-DiDiKTa obtained in toluene (1.01 × 10^{-5} M) at 300 K. (b) Solvatochromic absorption study of (rac)-Hel-DiDiKTa.

Figure S9. SS PL spectra of (rac)-Hel-DiDiKTa in toluene obtained in air and under N\textsubscript{2} at 300 K, λ\textsubscript{exc} = 350 nm.
Figure S10. (a) SS PL spectra of (rac)-Hel-DiDiKTa in mCP in air and under vacuum at 300 K, $\lambda_{\text{exc}} = 350$ nm. (b) Time-resolved PL of 1 wt% (rac)-Hel-DiDiKTa in mCP in air and under vacuum at 300 K, $\lambda_{\text{exc}} = 378$ nm.

Table S1. Summary of solvatochromic PL properties of (rac)-Hel-DiDiKTa.

| Solvent       | $\lambda_{\text{PL}}^{a}$ | FWHM $^{b}$ |
|---------------|---------------------------|-------------|
|               | nm                        | nm / eV     |
| Hexane (Hex)  | 452                       | 42 / 0.25   |
| Toluene (Tol) | 463                       | 44 / 0.26   |
| Ethyl acetate (EA) | 464                  | 50 / 0.28   |
| THF           | 467                       | 50 / 0.28   |
| CHCl$_3$      | 470                       | 50 / 0.28   |

$^{a}$Peak value of PL spectra obtained under aerated conditions at 300 K, concentration $1 \times 10^{-5}$ M, $\lambda_{\text{exc}} = 350$ nm. $^{b}$Full width at half maximum of the corresponding PL spectra.
Table S2. PLQY ($\Phi_{PL}$) study of (rac)-Hel-DiDiKTa at different doping concentration in mCP, $\lambda_{exc} = 350$ nm.

| Doping concentration / % | $\Phi_{PL}(N_2)$ / % | $\Phi_{PL}$(air) / % |
|--------------------------|-----------------------|----------------------|
| 3                        | 5                     | 5                    |
| 10                       | 4                     | 4                    |
| 30                       | 4                     | 4                    |
| 50                       | 5                     | 4                    |
| Neat film                | 4                     | 4                    |

Figure S11. Steady state PL spectrum at RT and at 77 K of (rac)-Hel-DiDiKTa in 1 wt% PMMA. $\lambda_{exc} = 350$ nm.

Figure S12. Temperature-dependent PL study of 1 wt% (rac)-Hel-DiDiKTa in mCP (a) non-normalized spectra, and (b) normalized spectra, $\lambda_{exc} = 350$ nm.
Table S3. $S_1$, $T_1$ and $\Delta E_{ST}$ values of (rac)-Hel-DiDiKTa obtained from the onsets of the prompt fluorescence and phosphorescence in different media.

|          | $S_1$ / eV | $T_1$ / eV | $\Delta E_{ST}$ / eV | $S_1$ / eV | $T_1$ / eV | $\Delta E_{ST}$ / eV | $S_1$ / eV | $T_1$ / eV | $\Delta E_{ST}$ / eV |
|----------|------------|------------|----------------------|------------|------------|----------------------|------------|------------|----------------------|
| a In toluene | 2.77       | 2.51       | 0.26                 | 2.78       | 2.52       | 0.26                 | 2.76       | 2.53       | 0.23                 |
| b 1 wt% in mCP |           |            |                      |            |            |                      |            |            |                      |
| c 1 wt% in PMMA |            |            |                      |            |            |                      |            |            |                      |

$^{a}$ $S_1$, $T_1$ and $\Delta E_{ST}$ values of (rac)-Hel-DiDiKTa calculated from the onsets of the prompt fluorescence and phosphorescence spectra in toluene glass at 77 K. $^{b}$ in 1 wt% (rac)-Hel-DiDiKTa doped in mCP, $^{c}$ and in 1 wt% (rac)-Hel-DiDiKTa doped in PMMA.

Table S4. Temperature-dependent Transient PL decay data of 1 wt% (rac)-Hel-DiDiKTa doped into mCP matrix.$^{a}$

| Temperature | $\tau_1$ / ns | $\tau_2$ / ns | $\tau_3$ / ns | $A_1$ | $A_2$ | $A_3$ | $R_1$ % | $R_2$ % | $R_3$ % |
|-------------|---------------|---------------|---------------|-------|-------|-------|--------|--------|--------|
| 300K        | 134           | 1408          | 7629          | 322   | 86    | 29    | 11.2   | 31.5   | 57.3   |
| 250K        | 75            | 2196          | 15985         | 454   | 88    | 63    | 2.8    | 15.6   | 81.7   |
| 200K        | 32            | 368           | 24142         | 1345  | 97    | 74    | 2.3    | 1.9    | 95.8   |
| 150K        | 28.6          | 1565          | -             | 295   | 4.4   | -     | 55     | 45     | -      |

$^{a}$ The transient PL decay data were fitted by triple-exponential function, where $A_i$ is the pre-exponential for lifetime $\tau_i$. $R_i$ is individual component ratio for prompt and delayed fluorescence. $R_i = \tau_i A_i / \Sigma \tau_i A_i$.

Determination of photophysical parameters

The efficiencies ($\Phi_p$ and $\Phi_d$) and constants ($k_p$ and $k_d$) for prompt and delayed emission can be estimated according to their contributions to total $\Phi_{PL}$ and their lifetimes ($\tau_p$ and $\tau_d$) according to the triple exponential fitting of time-resolved decay curves at 300 K.

To determine the rates, we used the following equations according to previous studies$^{[17]}$ of TADF photophysical processes:

\[ \Phi_{ISC} = \frac{\Phi_d / \Phi_p}{1 + \Phi_d / \Phi_p} \]  
(1)

\[ \Phi_{RISC} = \frac{k_{RISC}}{k_{RISC} + k_{HR} T} \]  
(2)

\[ k_p = \frac{\Phi_p}{\tau_p} \]  
(3)

\[ k_d = \frac{\Phi_d}{\tau_d} \]  
(4)

\[ k_r^S = \Phi_p \times k_p \]  
(5)
\[ k_{\text{ISC}} = \frac{\Phi_{\text{ISC}}}{\tau_p} \]  
\[ k_{\text{RISC}} = \frac{k_p \times k_d}{\text{klSC}} \left( \frac{\Phi_d}{\Phi_p} \right) \]  
\[ k_{\text{nr}}^T = k_d - (1 - \frac{k_{\text{ISC}}}{k_p}) \times k_{\text{RISC}} = k_d - (1 - \frac{k_{\text{ISC}}}{k_p}) \times \frac{k_d \times k_p \times \Phi_d}{\text{klSC} \times \Phi_p} \]

where \( \Phi_{\text{PL}} \) is the absolute \( \Phi_{\text{PL}} \); \( \Phi_p \) and \( \Phi_d \) are the prompt and delayed fluorescence efficiencies, respectively; \( k_p \) and \( k_d \) are the prompt and delayed fluorescence decay rate, respectively; \( \tau_p \) and \( \tau_d \) are the lifetimes of prompt and delayed fluorescence; \( \text{nr, ISC and RISC} \) are non-radiative conversion, intersystem crossing and reverse intersystem crossing processes.

**Table S5.** Photophysical properties of 1 wt% (rac)-Hel-DiDiKTa doped into mCP matrix at 300 K

| Temperature /K | \( \tau_p \)^a | \( \tau_d \)^b | \( k_p \)^c | \( k_d \)^d | \( k_{\text{ISC}} \)^f | \( k_{\text{RISC}} \)^g | \( k_{\text{nr}}^T \)^h | \( \Phi_{\text{RISC}} \)^i |
|---------------|----------------|----------------|-------------|-------------|----------------|----------------|----------------|----------------|
| 300           | 134            | 5.43           | 4.18        | 0.818       | 0.234          | 0.66           | 4.1            | 0.82           | 4.5            |

\( a) \) lifetime of prompt emission; \( b) \) lifetime of delayed emission; \( c) \) decay rate constant of prompt emission; \( d) \) decay rate constant of delayed emission; \( f) \) radiative decay rate constant of singlet excitons; \( g) \) intersystem crossing rate constant; \( h) \) reverse intersystem crossing rate constant; \( i) \) nonradiative decay rate constant of triplet excitons; \( i) \) percentage of reverse intersystem crossing.

**Figure S13.** Time-resolved PL of 1 wt% (rac)-Hel-DiDiKTa in mCP under vacuum at 77 K, \( \lambda_{\text{exc}} = 378 \) nm.
Table S6. Electrochemical data of (rac)-Hel-DiDiKTa compared to the parent DiKTa.[2]

| Compound            | $E_{\text{ox}}$  | $E_{\text{red}}$ | $E_{\text{HOMO}}^{b}$ | $E_{\text{LUMO}}^{b}$ | $\Delta E^{c}$ |
|---------------------|------------------|------------------|-----------------------|-----------------------|----------------|
| (rac)-Hel-DiDiKTa   | 1.81             | -1.16            | -6.15                 | -3.18                 | 2.97           |
| DiKTa               | 1.66[2]          | -1.33[2]         | -5.93[2]              | -3.11[2]              | 2.82[2]       |

a) Potential values obtained for (rac)-Hel-DiDiKTa from the DPV peak values, measured in degassed dichloromethane with 0.1 M [$n$Bu$_4$N]PF$_6$ as the supporting electrolyte and referenced with respect to SCE (Fc/Fc$^+$ = 0.46 eV).[18] b) HOMO and LUMO energy levels determined using the relation $E_{\text{HOMO/LUMO}} = - (E_{\text{ox/Red}} / E_{\text{ox/Red}} + 4.8)$ eV (using Fc/Fc$^+$ as the internal reference).[19] c) $\Delta E = | E_{\text{HOMO}} - E_{\text{LUMO}} |$ eV. [2] Value obtained from the literature in MeCN.

Resolution of (rac)-Hel-DiDiKTa.

Enantiomers were isolated using a Chiralpak IE column (10 mm I.D. x 250 mm) with Toluene:EtOAc 60:40 mobile phase and 5.0 mL min$^{-1}$ flow rate on a recycling HPLC system (Japan Analytical Industry LC-908 HPLC) for 3 cycles and then collected (Figure S14). The first enantiomer initially exhibited a retention time of 9.9 min while the second enantiomer exhibited a retention time of 11.5 min. Following separation, the purity of both samples was further checked by cHPLC and UV-Vis absorption, showing high purity for each enantiomer (Figures S15 and S16). Enantiomers exhibited enantiomeric ratios of (e.r.) > 99 % and > 97 % for (P) and (M) enantiomers, respectively and identical UV-Vis spectra at a concentration $\sim$ 5×10$^{-5}$ M in toluene.
Figure S14. Chiral-HPLC trace of (rac)-Hel-DiDiKTa. In blue, recycled signals submitted to the next cHPLC cycle. In orange, collected peaks. Both enantiomeric peaks were collected on the third cHPLC cycle.

Figure S15. cHPLC traces for (P)-Hel-DiDiKTa (left) and (M)-Hel-DiDiKTa (right). After 2 cycles, no significant impurity signals were found.
Figure S16. UV-Vis (left) and normalized UV-Vis (right) spectra of (P)-Hel-DiDiKTa and (M)-Hel-DiDiKTa in toluene ($\sim 5 \times 10^{-5}$ M).

**Chiroptical spectroscopy**

Circular-dichroism spectra were recorded in toluene at a concentration $\sim 2.25 \times 10^{-5}$ M (Figure S17) using a Chirascan (Applied Photophysics) spectrophotometer. The absorption dissymmetry factors ($g_{abs}$) values were obtained according to the following equation:

$$g_{abs} = \frac{A_L - A_R}{\frac{1}{2}(A_L + A_R)}$$

where $A_L$ and $A_R$ represent the magnitude of absorbed left- and right-handed light, respectively.

Circularly polarized photoluminescence (CPPL) measurements were performed using a homemade spectrofluoropolarimeter\cite{20} in toluene at a concentration of $\sim 5 \times 10^{-6}$ M. The samples were excited by 365 nm radiation (LED source) with a 90° geometry between excitation and detection channels. The excitation light was linearly polarized in the same plane as detection. Parameters used: band with 10 nm, scan speed 1 nm sec$^{-1}$, integration time 4 sec, PMT voltage 700 V, accumulations 10. The $g_{PL}$ factor is fairly constant throughout the emission band (Figure S18) and it was quantitatively estimated as the ratio between the integral of CPL spectrum over the integral of total fluorescence.
**Figure S17.** CD spectra (left) and $g_{abs}$ vs. wavelength (right) of $(P)$-Hel-DiDiKTa and $(M)$-Hel-DiDiKTa in toluene (~$2.25 \times 10^{-5}$ M).

**Figure S18.** $g_{PL}$ vs. wavelength of $(P)$-Hel-DiDiKTa and $(M)$-Hel-DiDiKTa in toluene (~$5 \times 10^{-6}$ M).

**Quantum chemical calculations**

The calculations were performed with the Gaussian 16 revision A_03\textsuperscript{[21]} suite for the density functional theory (DFT) and with the Turbomole/7.4\textsuperscript{[22]} package for SCS-CC2 calculations. Ground-state optimized structures were calculated using the PBE0 functional\textsuperscript{[23]} and the 6-31G(d,p) basis set.\textsuperscript{[24]} Ground state calculations were also performed with CAM-B3LYP,\textsuperscript{[25]} B3LYP,\textsuperscript{[26]} LCwPBE\textsuperscript{[27]} and M062X\textsuperscript{[28]} functionals at the same basis set. Excited state calculations were performed for each within the Tamm-Dancoff approximation (TDA). Molecular orbitals were visualized using GaussView 5.0 software.\textsuperscript{[29]} Spin-component scaling coupled-cluster singles-and-doubles model (SCS-CC2) was also used in conjunction with cc-
pVDZ basis set. We first optimized the ground state using SCS-CC2 method, then vertical excited states were performed on the ground state optimized structure using the SCS-CC2 method. Difference density plots were used to visualize change in electronic density between the ground and excited state and were visualized using the VESTA package.

Figure S19. Ground state energy and pictures of Hel-DiDiKTa and QA-2 calculated at PBE0/6-31 G(d,p).
Table S7. Overall energy of QA-2 and Hel-DiDiKTa in the gas phase using various methods, DFT used 6-31G(d,p) and SCS-CC2 used cc-pVDZ basis set.

| Method       | QA-2 energy / kJ mol⁻¹ | Hel-DiDiKTa energy / kJ mol⁻¹ | Δ_energy / kJ mol⁻¹ᵃ |
|--------------|------------------------|-------------------------------|----------------------|
| CAMB3LYP     | -4502671               | -4502642                      | -29                  |
| LCoPBE       | -4501739               | -4501714                      | -25                  |
| B3LYP        | -4505176               | -4505149                      | -26                  |
| PBE0         | -4499935               | -4499907                      | -29                  |
| M062X        | -4503030               | -4503003                      | -27                  |
| SCS-CC2      | -4491500               | -4491482                      | -18                  |

ᵃ)(Energy of QA-2 – Energy of Hel-DiDiKTa)

Figure S20. Double electronic excited state difference density plot of Hel-DiDiKTa and vertical excited state energies of it and the parent DiKTa (dashed red line).
Table S8. Computational data calculated in the gas phase for Hel-DiDiKTa, DiKTa and previously mentioned CPL-active triangulene, Hel-DiKTa-2.[32]

| Compound        | HOMO / eV | LUMO / eV | ΔE / eV | S1 / eV (f) | T1 / eV | T2 / eV | ΔE_ST / eV |
|-----------------|-----------|-----------|---------|-------------|---------|---------|------------|
| DiKTa           | -6.20     | -2.23     | 3.97    | 3.45 (0.20) | 3.18    | 3.60    | 0.27       |
| Hel-DiDiKTa     | -6.26     | -2.53     | 3.73    | 3.34 (0.13) | 3.10    | 3.22    | 0.24       |
| Hel-DiKTa-2     | -5.90     | -2.24     | 3.66    | 3.29 (0.21) | 2.79    | 3.07    | 0.51       |

Figure S21. Double electronic excited state difference density plot of Hel-DiKTa-2 and vertical excited state energies of it and the parent DiKTa (in dashed red lines).
Figure S22. HOMO/LUMO electron density pictures and energies of the DiKTa, Hel-DiDiKTa and Hel-DikTa-2 in the gas phase calculated with PBE0/6-31g(d,p), isovalue = 0.02.
Figure S23. Simulated absorption spectra of Hel-DiDiKTa considering first 8 singlet excited states (a) and orbital levels of calculated singlet states and relevant important difference density plots (b), calculated at SCS-CC2/cc-pVDZ.

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