Structural and Photophysical Properties of Various Polypyridyl Ligands: A Combined Experimental and Computational Study

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S1 Experimental details

S1.1 General

Reagents and solvents were purchased from common chemical suppliers and used without further purification. Before use, zinc dust was activated by treating it with 1 M aqueous HCl solution, then it was washed with distilled water, ethanol and diethyl ether. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III HD 400 spectrometer at 25°C. Chemical shifts (ν) are reported in parts per million (ppm) relative to tetramethylsilane (ν = 0) using the residual solvent peak as internal reference (CDCl₃ δ_H = 7.26 and δ_C = 77.16). Mass spectrometry (low resolution) was performed on an Agilent 1100 Series MSD SL mass spectrometer with electrospray ionisation (ESI, 4000 V, 70 eV) and with a single quadrupole detector. UV-Vis spectra were recorded using a Shimadzu UV-1650 PC spectrophotometer at 20°C. Samples at concentrations of 10⁻³–10⁻⁵ M were prepared in HPLC grade acetonitrile and were measured in a quartz cuvette with path length 1.0 cm. Acetonitrile is a polar apotic solvent with a relative permittivity ε_r = 37.5. The transmission was detected and converted to absorbance. Absorbance spectra were acquired in the range of 220–900 nm, with a step size of 0.5 nm.

S1.2 Synthetic procedures and characterization data

S1.2.1 2,2'-bipyridine-5,5'-dicarbonitrile

2,2'-bipyridine-5,5'-dicarbonitrile was synthesized according to a slightly adapted procedure reported by Duan et al.[1] 5 mol% NiCl₂•6H₂O (180 mg, 0.75 mmol) was dissolved in 35 mL DMF under argon atmosphere. The resulting mixture was heated to 40°C, after which 2-bromo-5-cyanopyridine (2.75 g, 15.0 mmol), anhydrous LiCl (0.64 g, 15.0 mmol, 1 eq) and activated zinc dust (1.18 g, 18.0 mmol, 1.2 eq) were added. The temperature was raised to 50°C, and
an iodine grain and two drops of acetic acid were added into the mixture, which was then stirred for 30 min to complete the conversion. Subsequently, the mixture was cooled to 0°C before adding 1 M HCl (15 mL) and stirring it for an additional 30 min. Hereafter, the reaction mixture was made alkaline with aqueous ammonia (25 wt%), and the resulting product was extracted with ethyl acetate (3 x 50 mL). The combined organic fractions were washed with a 5 wt% aqueous LiCl solution and dried over MgSO₄, filtered and concentrated. 2,2’-bipyridine-5,5’-dicarbonitrile was obtained as a beige powder (1.55 g, 91%). An analytical pure, white product was obtained after automated reverse phase flash chromatography (C18) using acetonitrile and water as eluent.

\[ \text{H NMR (400 MHz, CDCl₃):} \delta \text{H} 8.14 (2H, dxd, } J = 8.3, 2.0 \text{ Hz, H}^{4/4'}, 8.64 (2H, dxd, } J = 8.3, 0.8 \text{ Hz, H}^{3/3'}, 8.97 (2H, dxd, } J = 2.0, 0.8 \text{ Hz, H}^{6/6'} \). \[ \text{C NMR (100.6 MHz, CDCl₃):} \delta \text{C} 110.7 (C^{5/5'}), 116.5 (C≡N) 121.7 (C^{3/3'}), 140.5 (C^{4/4'}), 152.1 (C^{6/6'}), 157.0 (C^{2/2'}). \] MS (ESI, 70 eV) m/z (%): 207.0 ([M + H]⁺, 100). The spectroscopic data are in agreement with the previously reported literature values [2].

**Figure S2:** ¹H NMR of 2,2’-bipyridine-5,5’-dicarbonitrile

**13C NMR**
Figure S3: $^{13}$C NMR of 2,2'-bipyridine-5,5'-dicarbonitrile

S1.2.2 5,5'-dibromo-2,2'-bipyridine

The synthetic procedure of 5,5'-dibromo-2,2'-bipyridine (4 in Figure S4) was based on the method reported by D'Souza et al [3]. A solution of 2,2'-bipyridine (5.00 g, 3.20 mmol) in methanol (30 mL) was treated with an aqueous HBr solution (48 wt% in H$_2$O, 7.4 mL, 6.56 mmol, 2.05 eq) at 0°C. After addition, the reaction mixture was warmed up to room temperature and stirred for 20 minutes at room temperature. Subsequently, the solvent was evaporated in vacuo and the residue was further thoroughly dried under high vacuum to obtain 2,2'-bipyridine hydrobromide salt (10.18 g, quant.) as a light-yellow powder. A 10 mL pressure resistant vial of Pyrex glass was charged with finely grounded 2,2'-bipyridine hydrobromide (3 in Figure S4) (2.75 g, 8.65 mmol) and cooled to 0°C. Subsequently, bromine (1.33 mL, 25.94 mmol, 3 eq) was slowly added using a disposable plastic syringe with a long needle, making sure that the tip of the needle was digging into the 2,2'-bipyridine hydrobromide powder. After screwing the cap tightly onto the pressure resistant vial, the temperature was raised to 170°C for 72 h. Subsequently, the vial was cooled to 0°C in an ice bath before opening it. (Caution: wear protective clothing and be aware that HBr gas can escape when loosening the cap). The hard lump of crude product was crumbled with a spatula and the powder was transferred into a 500 mL flask containing 50 mL NaOH (1 M), 3.0 g Na$_2$SO$_3$ and 100 mL CHCl$_3$. The mixture was stirred at room temperature until complete dissolving. The organic phase was separated, and the aqueous phase was extracted twice with CHCl$_3$ (2 x 15 mL). The combined organic phases were dried over MgSO$_4$, filtered and evaporated. The crude product was purified by recrystallization from DMF-ethanol. 5,5'-dibromo-2,2'-bipyridine was obtained as thin colorless needles (1.03 g, 40%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ 7.94 (2H, dxd, $J = 8.5$, 2.2 Hz, H$_{4/4'}$), 8.29 (2H, d, $J = 8.5$
Hz, \( H^{3/3'} \), 8.71 (2H, d, \( J = 2.2 \text{ Hz}, H^{6/6'} \)). 13C NMR (100.6 MHz, CDCl3): \( \delta_{C} 121.6 (C^{5/5'}), 122.4 (C^{3/3'}), 139.8 (C^{4/4'}), 150.4 (C^{6/6'}), 153.8 (C^{2/2'}) \). MS (ESI, 70 eV) m/z (%): 314.8 ([M + H]+, 100).

The spectroscopic data are in agreement with the previously reported literature values [3]. 1H NMR

Figure S5: 1H NMR of 5,5’-dibromo-2,2’-bipyridine

13C NMR

Figure S6: 13C NMR of 5,5’-dibromo-2,2’-bipyridine
5,5'-bis(4-cyanophenyl)-2,2'-bipyridine

Figure S7: Synthesis of 5,5'-bis(4-cyanophenyl)-2,2'-bipyridine.

5,5'-dibromo-2,2'-bipyridine (4 in Figure S7) (2.00 g, 6.4 mmol), 4-cyanoboronic acid (2.34 g, 15.9 mmol, 2.5 eq), Pd(PPh₃)₄ (294 mg, 0.25 mmol, 4 mol%) and K₂CO₃ (4.40 g, 31.85 mmol, 5 eq) were loaded into a 2-neck flask (250 mL) equipped with a condenser and two rubber septa, and placed under argon atmosphere. Degassed dioxane (100 mL) and degassed water (20 mL) were added, after which the yellow solution was heated to 90°C for 24 h. After cooling to room temperature, the precipitate was filtered and washed with water, THF and chloroform to afford 5,5'-bis(4-cyanophenyl)-2,2'-bipyridine (5 in Figure S7) as an off-white powder (2.10 g, 92%).

$^1$H NMR (400 MHz, CDCl₃): $\delta_H$ 7.76-7.83 (8H, m, CHarom), 8.07 (2H, dxd, $J = 8.3, 2.4$ Hz, H$_{4/4}''$), 8.59 (2H, d, $J = 8.3$ Hz, H$_{3/3}''$), 8.95 (2H, d, $J = 2.2$ Hz, H$_{6/6}''$). The compound was not sufficiently soluble to record an adequate $^{13}$C NMR spectrum. MS (ESI, 70 eV) m/z (%): 359.1 ([M + H]$^+$, 100). $^1$H NMR

Figure S8: $^1$H NMR 5,5'-bis(4-cyanophenyl)-2,2'-bipyridine

S2 Electric-dipole allowed transitions

The propagator, and thus the probability, of the transition between two states is defined as follows:

$$P = \int d\tau \Psi^* \hat{\rho} \Psi,$$

(1)
with $\hat{\mu}$ the electric dipole moment operator and $\\Psi$ and $\\Psi'$ the wavefunctions of the initial and final state respectively [4]. If the direct product does not contain the totally symmetric representation, the transition is said to be electric-dipole forbidden. Therefore, in order for the transition to be allowed, the following condition has to be fulfilled:

$$\Gamma(\\Psi') \times \Gamma(\\mu) \times \Gamma(\\Psi) = A,$$  \hspace{1cm} (2)

where $\Gamma$ stands for ‘symmetry species of’ and $A$ denotes the totally symmetric species of the point group. If the product of two symmetry species is totally symmetric, those species must have the same symmetry. Therefore, equation (2) can be rewritten as follows:

$$\Gamma(\\Psi') \times \Gamma(\\Psi) = \Gamma(\\mu).$$  \hspace{1cm} (3)

Furthermore, as the ground state is a closed shell system, this becomes

$$\Gamma(\\Psi') = \Gamma(\\mu).$$  \hspace{1cm} (4)

**S3  Ground state properties of polypyridyl ligands**

|       | (1)  | (2)  | (3)  | (4)  | (5)  | (6)  |
|-------|------|------|------|------|------|------|
| LUMO+3| 0.383| 0.070| 0.326| -1.269| -1.897| -1.275|
| LUMO+2| -0.118| -0.205| -0.531| -1.338| -1.945| -1.415|
| LUMO+1| -0.745| -1.457| -1.070| -1.750| -2.177| -1.943|
| LUMO  | -1.132| -2.065| -1.687| -2.937| -3.025| -2.553|
| HOMO  | -7.440| -7.819| -7.008| -7.292| -6.954| -6.488|
| HOMO-1| -7.425| -7.858| -7.510| -7.787| -7.442| -7.184|
| HOMO-2| -8.124| -8.544| -7.986| -8.229| -7.708| -7.451|
| HOMO-3| -10.105| -9.860| -8.160| -8.437| -7.865| -7.695|
| HOMO-4| -11.096| -10.404| -8.495| 8.627 | -7.896| -7.702|
| HOMO-5| -11.179| -10.653| -8.712| -8.701| -8.026| -7.764|
| HOMO-9| -14.548| -12.635| -11.331| -10.666| -8.377| -8.786|

$\pi_{AQ}, \pi_{Q}, n, \pi_{AQ}$ orbitals of linkers (1)-(6) in eV. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Table S2: Optimized bond distances [Å] and angles [°] for the ground state of the trans configuration of linker (4) for the B3LYP and M06 functional. The numbering of the atoms is given in the left pane of Figure S9. Calculations carried out with the 6-31++G** basis set.

![Figure S9: The numbering of atoms for the trans (left) and cis (right) conformer of linker (4).](image)

| Parameter       | B3LYP | M06 |
|-----------------|-------|-----|
| C1C1'           | 1.49  | 1.48|
| C1N1            | 1.35  | 1.34|
| N1C3            | 1.33  | 1.32|
| C3C4            | 1.41  | 1.40|
| C4C5            | 1.40  | 1.40|
| C5C2            | 1.39  | 1.38|
| C2C1            | 1.40  | 1.40|
| C2H1            | 1.08  | 1.08|
| C3H2            | 1.09  | 1.09|
| C5H3            | 1.08  | 1.09|
| C4C6            | 1.43  | 1.43|
| C6N2            | 1.16  | 1.16|
| C1N1C3          | 118.7 | 118.6|
| N1C3C4          | 122.8 | 122.8|
| C3C4C5          | 118.6 | 118.6|
| C4C5C2          | 118.5 | 118.5|
| C5C2C1          | 119.0 | 118.9|
| C2C1N1          | 122.4 | 122.6|
| N1C1C1’N1’      | 180.0 | 180.0|

Table S3: Theoretical values of $\phi_{\text{cis}}$, $E_{\text{cis}}$, $E_{\text{trans-cis}}$, and $E_{\text{cis-trans}}$ found in literature for linker (3). $^a$ Optimization has been performed at the HF/6-31G** level followed by single point calculations at the MP2/6-31G**.

| Level of theory | $\phi_{\text{cis}}$ | $E_{\text{cis}}$ | $E_{\text{trans-cis}}$ | $E_{\text{cis-trans}}$ |
|-----------------|---------------------|-----------------|------------------------|------------------------|
| [5]BP86/TZVP at 298.15K | 38               | 26.8           | 32.6                   | 5.8                    |
| [6]BPW91/6-31G*  | 38.16             | 26.38          | 31.21                  | 4.83                   |
| [6]B3LYP/6-31G*  | 39.54             | 27.16          | 31.00                  | 3.84                   |
| [7]HF//MP2/6-31G** | 44.9            | 24.8           | 30.4                   | 5.6                    |
| [6]HF/6-31G*    | 43.51             | 27.6           | 30.86                  | 3.26                   |
| [6]MP2/6-31G*   | 43.65             | 26.34          | 30.52                  | 4.18                   |
S4  Excited state properties of polypyridyl ligands

Figure S10: UV-Vis spectra of ligand (4) for several basis sets (full lines) together with the experimental spectrum (dashed line). Calculations carried out with the B3LYP functional.

| Parameter       | B3LYP 6-31++G** | [6]HF 6-31G* | [6]B3LYP 6-31+G* | [6]BPW91 6-31+G* | [6]MP2 6-31G* |
|-----------------|-----------------|--------------|------------------|-------------------|----------------|
| C1C1'           | 1.49            | 1.49         | 1.49             | 1.49              | 1.48           |
| C1N1            | 1.34            | 1.32         | 1.35             | 1.36              | 1.35           |
| N1C3            | 1.33            | 1.32         | 1.34             | 1.34              | 1.34           |
| C3C4            | 1.39            | 1.38         | 1.40             | 1.40              | 1.40           |
| C4C5            | 1.39            |              |                  |                   |                |
| C5C2            | 1.39            |              |                  |                   |                |
| C2C1            | 1.40            |              |                  |                   |                |
| C2H1            | 1.08            |              |                  |                   |                |
| C3H2            | 1.09            |              |                  |                   |                |
| C5H3            | 1.09            |              |                  |                   |                |
| C1N1C3          | 118.2           | 118.8        | 118.3            | 117.9             | 117.6          |
| N1C3C4          | 123.6           | 123.5        | 123.6            | 123.9             | 123.6          |
| C3C4C5          | 118.0           |              |                  |                   |                |
| C4C5C2          | 119.0           |              |                  |                   |                |
| C5C2C1          | 118.9           |              |                  |                   |                |
| C2C1N1          | 122.3           |              |                  |                   |                |
| N1C1C1′N1′      | 180.0           | 180          | 180              | 180               | 180            |

Table S4: Optimized bond distances [Å] and angles [°] for the ground state of the trans configuration of linker (3) for several levels of theory. The same numbering of the atoms is used as for linker (4), which is given in the left pane of Figure S9.
| Functional   | $\Delta E_{\text{solvent}}$ |
|--------------|-----------------------------|
| PBE          | 8.17                        |
| B3LYP        | 7.73                        |
| M06          | 7.54                        |
| TPSSh        | 7.66                        |
| CAM-B3LYP    | 6.45                        |
| LC-ωHPBE     | 5.35                        |
| ωB97X-D      | 6.24                        |

Table S5: $\Delta E_{\text{solvent}}$, i.e., the energy shift between the strongest absorption peak of the trans structure with and without the inclusion of solvent, of linker (4) for different functionals. Calculations performed with the 6-31++G** basis set.

| Parameter   | ground state | 1$^{st}$ non-dark | 1$^{st}$ bright | 1$^{st}$ dark | 2$^{nd}$ bright |
|-------------|--------------|-------------------|----------------|--------------|----------------|
| C1C1'       | 1.49         | 1.43              | 1.42           | 1.45         | 1.44           |
| C1N1        | 1.40         | 1.43              | 1.43           | 1.36         | 1.42           |
| N1C3        | 1.39         | 1.37              | 1.37           | 1.33         | 1.40           |
| C3C4        | 1.40         | 1.43              | 1.43           | 1.41         | 1.43           |
| C4C5        | 1.41         | 1.42              | 1.41           | 1.42         | 1.41           |
| C5C2        | 1.33         | 1.30              | 1.31           | 1.38         | 1.34           |
| C2C1        | 1.35         | 1.35              | 1.37           | 1.42         | 1.37           |
| C2H1        | 1.08         | 1.09              | 1.08           | 1.08         | 1.08           |
| C3H2        | 1.08         | 1.09              | 1.08           | 1.09         | 1.09           |
| C5H3        | 1.09         | 1.09              | 1.09           | 1.08         | 1.09           |
| C4C6        | 1.43         | 1.41              | 1.42           | 1.42         | 1.41           |
| C6N2        | 1.16         | 1.17              | 1.17           | 1.17         | 1.17           |
| C1N1C3      | 119.0        | 120.6             | 120.1          | 119.4        | 119.5          |
| N1C3C4      | 118.5        | 120.1             | 120.4          | 123.1        | 119.1          |
| C3C4C5      | 118.6        | 116.8             | 117.5          | 117.7        | 117.6          |
| C4C5C2      | 122.8        | 120.6             | 120.4          | 119.3        | 123.4          |
| C5C2C1      | 118.7        | 125.4             | 125.2          | 119.2        | 119.7          |
| C2C1N1      | 122.4        | 116.6             | 116.4          | 121.3        | 120.8          |
| N1C1C1'N1'  | 180.0        | 180.0             | 180.0          | 180.0        | 180.0          |

Table S6: Optimized bond distances [Å] and angles [°] for the ground, two bright, first non-dark and first dark excitations of the trans conformer of linker (4). The numbering of the atoms is given in the left pane of Figure S9. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Figure S11: Visualization of the important orbitals of linker (3). The arrows indicate the most dominant contributions of the first three singlet excitations, characterized by the excitation energy in nm, oscillator strength, \( f \), between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO, HOMO-1 and HOMO-4 in descending order. The unoccupied MOs in the right represent respectively the LUMO+2 and LUMO. This labeling is conform the binding energies taken up in Table S1. The meaning of the colors and the style of the arrows is outlined in the text. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S12: Visualization of the important orbitals of linker (5). The arrows indicate the most dominant contributions of the first three singlet excitations, characterized by the excitation energy in nm, oscillator strength, \( f \), between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO, HOMO-1 and HOMO-9 in descending order. The unoccupied MOs in the right represent respectively the LUMO+3 and LUMO. This labeling is conform the binding energies taken up in Table S1. The meaning of the colors and the style of the arrows is outlined in the text. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Figure S13: Visualization of the important orbitals of linker (6). The arrows indicate the most dominant contributions of the bright excitation, characterized by the excitation energy in nm, oscillator strength, $f$, between brackets. The occupied MO in the left represents the whereas the unoccupied MO in the right represents the LUMO. This labeling is conform the binding energies taken up in Table S1. The meaning of the colors and the style of the arrows is outlined in the text. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S14: Visualization of the HOMO and LUMO of linker (4) with a dihedral angle of 92°. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S15: Visualization of the important orbitals of the cis conformer of linker (4). The arrows indicate the most dominant contributions of the first three singlet excitations, characterized by the excitation energy in nm, oscillator strength, $f$, between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO, HOMO-1 and HOMO-4 in descending order. The unoccupied MOs in the right represent respectively the LUMO+1 and LUMO. The meaning of the colors and the style of the arrows is outlined in the text. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
| Parameter        | ground state | 1<sup>st</sup> non-dark | 1<sup>st</sup> bright | 2<sup>nd</sup> bright |
|------------------|--------------|-------------------------|-----------------------|-----------------------|
| C1C1'            | 1.49         | 1.41                    | 1.42                  | 1.45                  |
| C1N1             | 1.40         | 1.42                    | 1.45                  | 1.39                  |
| N1C3             | 1.39         | 1.38                    | 1.37                  | 1.42                  |
| C3C4             | 1.40         | 1.43                    | 1.42                  | 1.40                  |
| C4C5             | 1.41         | 1.42                    | 1.44                  | 1.42                  |
| C5C2             | 1.33         | 1.30                    | 1.31                  | 1.34                  |
| C2C1             | 1.35         | 1.37                    | 1.39                  | 1.34                  |
| C2H1             | 1.08         | 1.08                    | 1.08                  | 1.08                  |
| C3H2             | 1.08         | 1.08                    | 1.08                  | 1.08                  |
| C5H3             | 1.09         | 1.09                    | 1.09                  | 1.08                  |
| C4C6             | 1.43         | 1.41                    | 1.41                  | 1.43                  |
| C6N2             | 1.16         | 1.170                   | 1.17                  | 1.16                  |
| C1N1C3           | 119.2        | 119.4                   | 120.5                 | 117.6                 |
| N1C3C4           | 118.3        | 120.6                   | 118.4                 | 119.2                 |
| C3C4C5           | 118.6        | 117.5                   | 117.9                 | 120.7                 |
| C4C5C2           | 123.0        | 119.9                   | 124.3                 | 117.3                 |
| C5C2C1           | 118.5        | 125.0                   | 118.6                 | 123.8                 |
| C2C1N1           | 122.4        | 117.6                   | 120.3                 | 121.4                 |
| N1C1C1'N1'       | -32.4        | -0.1                    | -1.34                 | -0.01                 |

Table S7: Optimized bond distances [Å] and angles [°] for the ground, two bright and first non-dark excitations of the cis conformer of linker (4). The numbering of the atoms is given in the right pane of Figure S9. Calculations carried out at the B3LYP/6-31+G** level of theory and with acetonitrile as solvent.
Figure S16: Energy of the LUMO and HOMO of linker (4) as a function of the dihedral angle. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Figure S17: Influence of the dihedral angle on the UV-Vis spectrum of linker (3). Experimental result is indicated with a dashed line. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S18: Influence of the dihedral angle on the UV-Vis spectrum of linker (5). Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Figure S19: Influence of the dihedral angle on the UV-Vis spectrum of linker (6). Experimental result is indicated with a dashed line. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S20: Influence of the dihedral angle on the UV-Vis spectrum of linker (7). Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
We also apply some dynamic approaches in this investigation. MD simulations have been performed starting from the trans conformer. Snapshots are extracted during the simulation run and used as input structures for TDDFT calculations [8, 9]. As we expect, a broadening of the main absorption peak is observed due to the small spread in the dihedral angles. However, no better agreement with experiment is obtained. Only the height of the second peak increases slightly, which is in agreement with experiment. Furthermore, this peak also shifts to larger wavelengths.

![Figure S21: Influence of the dihedral angle on the UV-Vis spectrum of linker (8). Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.](image)

![Figure S22: Comparison of UV-Vis spectra of linker (4): black line represents spectrum obtained from snapshots of MD simulation starting from trans conformer, green dotted line corresponds to UV-Vis spectrum of the trans conformer and the experimental result is presented with a green dotted line. Dynamical and static calculations carried out at the BLYP and B3LYP level of theory respectively.](image)
**S5** Other ligands

Figure S23: Visualization of the important orbitals of linker (7). The arrows indicate the most dominant contributions of the two main absorption peaks, characterized by the excitation energy in nm, oscillator strength, $f$, between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO and HOMO-1 in descending order. The unoccupied MOs in the right represent respectively LUMO+2, LUMO+1, and LUMO. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S24: Visualization of the important orbitals of linker (8). The arrows indicate the most dominant contributions of the two main absorption peaks, characterized by the excitation energy in nm, oscillator strength, $f$, between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO and HOMO-1, HOMO-2, HOMO-3, and HOMO-4 in descending order. The unoccupied MOs in the right represent respectively LUMO+1 and LUMO. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Figure S25: Visualization of the important orbitals of linker (9). The arrows indicate the most dominant contributions of the two main absorption peaks, characterized by the excitation energy in nm, oscillator strength, \( f \), between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO, HOMO-2, HOMO-3, and HOMO-4 in descending order. The unoccupied MOs in the right represent respectively LUMO+2, LUMO+1, and LUMO.

Figure S26: Visualization of the important orbitals of linker (10). The arrows indicate the most dominant contributions of the two main absorption peaks, characterized by the excitation energy in nm, oscillator strength, \( f \), between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO, HOMO-3, and HOMO-4 in descending order. The unoccupied MOs in the right represent respectively LUMO+2, LUMO+1, and LUMO.
Figure S27: Visualization of the important orbitals of linker (11). The arrows indicate the most dominant contributions of the three main absorption peaks, characterized by the excitation energy in nm, oscillator strength, \( f \), between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO, HOMO-1, and HOMO-2 in descending order. The unoccupied MOs in the right represent respectively LUMO+3, LUMO+2, and LUMO. of Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S28: Visualization of the important orbitals of linker (12). The arrows indicate the most dominant contributions of the two main absorption peaks, characterized by the excitation energy in nm, oscillator strength, \( f \), between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO and HOMO-1 in descending order. The unoccupied MOs in the right represent respectively LUMO+1, and LUMO. of Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Figure S29: Visualization of the important orbitals of linker (13). The arrows indicate the most dominant contributions of the two main absorption peaks, characterized by the excitation energy in nm, oscillator strength, \( f \), between brackets, and amplitude in square brackets if more contributions are reported for a specific excitation. The occupied MOs in the left represent respectively the HOMO and HOMO-1 in descending order. The unoccupied MOs in the right represent respectively LUMO+1 and LUMO. Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Figure S30: Theoretical UV-Vis spectra of ligands (7) and (8). Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.
Table S8: Expansion of the wavefunction of HOMO and LUMO in atomic contributions of the nitrogen atoms in the rings for linkers (7) and (8). The highlighted values show that the HOMO of ligand (8) does not have large contributions of these nitrogen atoms.
Figure S31: Theoretical UV-Vis spectra of ligand (12). Calculations carried out at the B3LYP/6-31++G** level of theory and with acetonitrile as solvent.

Table S9: Excitation energies [eV] and oscillator strengths for the first 30 singlet transitions of linkers (1)-(13). Calculations carried out at the B3LYP/6-311++G** level of theory and with acetonitrile as solvent.

| Linker (1) | Linker (2) | Linker (3) | Linker (4) | Linker (5) |
|-----------|-----------|-----------|-----------|-----------|
| 4.9535 f=0.0076 | 4.5629 f=0.0007 | 4.3874 f=0.0026 | 3.8148 f=0.0007 | 3.5082 f=1.4661 |
| 5.3090 f=0.0000 | 5.0498 f=0.0043 | 4.5902 f=0.0529 | 3.9834 f=1.0577 | 3.5210 f=0.0012 |
| 5.4163 f=0.1121 | 5.1744 f=0.1150 | 4.8019 f=0.0000 | 4.2408 f=0.0000 | 3.7849 f=0.0000 |
| 6.1863 f=0.0501 | 5.6100 f=0.2145 | 4.9191 f=0.0000 | 4.6517 f=0.0000 | 3.9411 f=0.0004 |
| 6.4679 f=0.0000 | 6.4387 f=0.3998 | 5.0717 f=0.0000 | 4.9124 f=0.0000 | 3.9940 f=0.0000 |
| 6.4793 f=0.0862 | 6.4888 f=0.0000 | 5.2729 f=0.0050 | 4.9982 f=0.0837 | 4.1733 f=0.0069 |
| 6.7974 f=0.7403 | 6.6432 f=0.0000 | 5.4554 f=0.0599 | 5.0676 f=0.0000 | 4.2707 f=0.0000 |
| 6.8112 f=0.7123 | 6.7859 f=0.2853 | 5.6910 f=0.0000 | 5.1490 f=0.0071 | 4.3212 f=0.0000 |
| 7.0285 f=0.0710 | 6.8026 f=0.0052 | 5.9850 f=0.0005 | 5.3412 f=0.0000 | 4.3702 f=0.0000 |
| 7.0914 f=0.0079 | 6.8684 f=0.0023 | 6.1571 f=0.1223 | 5.5308 f=0.0000 | 4.4784 f=0.0107 |
| 7.1652 f=0.0017 | 7.2266 f=0.3260 | 6.1770 f=0.0000 | 5.5817 f=0.0000 | 4.5103 f=0.0000 |
| 7.1986 f=0.0000 | 7.3863 f=0.0074 | 6.2067 f=0.0000 | 5.6783 f=0.1304 | 4.5230 f=0.0080 |
| 7.2377 f=0.0297 | 7.4336 f=0.0024 | 6.2701 f=0.0000 | 5.7371 f=0.0002 | 4.5811 f=0.0000 |
| 7.5674 f=0.0000 | 7.4911 f=0.0303 | 6.4253 f=0.5320 | 5.9767 f=0.0000 | 4.5880 f=0.0000 |
| 7.7761 f=0.0082 | 7.5301 f=0.0001 | 6.5251 f=0.0173 | 6.0067 f=0.0000 | 4.6556 f=0.0013 |
| 7.7851 f=0.0000 | 7.5389 f=0.0015 | 6.5320 f=0.0000 | 6.0710 f=0.0000 | 4.6561 f=0.0000 |
| 7.7908 f=0.0029 | 7.5528 f=0.0909 | 6.6568 f=0.0000 | 6.0817 f=0.0000 | 4.7473 f=0.1070 |
| 7.8461 f=0.0345 | 7.5869 f=0.0011 | 6.7287 f=0.0000 | 6.1019 f=0.1239 | 4.8195 f=0.0000 |
| 7.8909 f=0.0000 | 7.6201 f=0.0151 | 6.7606 f=0.0011 | 6.3070 f=0.3586 | 4.8352 f=0.0000 |
| 7.9615 f=0.0016 | 7.6420 f=0.0001 | 6.7989 f=0.0000 | 6.3616 f=0.0000 | 4.8397 f=0.0018 |
| 7.9954 f=0.0010 | 7.9103 f=0.0143 | 6.8584 f=0.3791 | 6.3752 f=0.0000 | 4.9876 f=0.0043 |
| 8.0119 f=0.0079 | 7.9964 f=0.0014 | 6.9630 f=0.0508 | 6.4055 f=0.0000 | 5.0240 f=0.0000 |
| Linker (6) | Linker (7) | Linker (8) | Linker (9) | Linker (10) |
|-----------|------------|------------|------------|-------------|
| 8.0966    | 8.0918     | 7.0424     | 6.4290     | 5.0803      |
| 8.1177    | 8.1168     | 7.0911     | 6.5647     | 5.1332      |
| 8.1784    | 8.1572     | 7.1256     | 6.6510     | 5.2207      |
| 8.4823    | 8.1592     | 7.1397     | 6.6518     | 5.2318      |
| 8.5677    | 8.1836     | 7.1782     | 6.6632     | 5.3060      |
| 8.6113    | 8.1838     | 7.1870     | 6.8108     | 5.3258      |
| 8.6923    | 8.1881     | 7.2378     | 6.8274     | 5.3431      |
| 8.7923    | 8.2219     | 7.3075     | 6.8295     | 5.4119      |
| 3.4848    | 3.5914     | 3.4189     | 3.8606     | 2.4774      |
| 3.9238    | 3.7333     | 3.8313     | 3.8803     | 2.8009      |
| 4.1606    | 3.7714     | 3.9398     | 3.9838     | 3.5180      |
| 4.3437    | 3.8299     | 3.9876     | 4.0023     | 3.5277      |
| 4.3740    | 3.9842     | 4.0832     | 4.2576     | 3.7664      |
| 4.4077    | 4.3006     | 4.2080     | 4.2874     | 3.7808      |
| 4.5483    | 4.4510     | 4.3714     | 4.2998     | 4.1012      |
| 4.5600    | 4.5440     | 4.5067     | 4.3508     | 4.1691      |
| 4.6927    | 4.6306     | 4.5195     | 4.4605     | 4.1913      |
| 4.7744    | 4.6547     | 4.5343     | 4.6548     | 4.4281      |
| 4.7831    | 4.7851     | 4.5954     | 4.6853     | 4.3526      |
| 4.8974    | 4.8590     | 4.6589     | 4.9202     | 4.3929      |
| 4.9806    | 4.9720     | 4.9586     | 4.9417     | 4.5902      |
| 4.9936    | 5.0134     | 4.9837     | 4.9762     | 4.6797      |
| 5.0243    | 5.0591     | 4.9890     | 5.0034     | 4.7553      |
| 5.0568    | 5.0646     | 5.0451     | 5.0119     | 4.7993      |
| 5.0689    | 5.1176     | 5.1930     | 5.0677     | 4.9127      |
| 5.2280    | 5.1362     | 5.2531     | 5.1008     | 4.9130      |
| 5.2854    | 5.2835     | 5.2933     | 5.1856     | 5.0533      |
| 5.3110    | 5.3324     | 5.3264     | 5.2666     | 5.0948      |
| 5.3323    | 5.4614     | 5.4570     | 5.4546     | 5.0972      |
| 5.3487    | 5.4945     | 5.4959     | 5.5273     | 5.1196      |
| 5.4458    | 5.5390     | 5.5313     | 5.5340     | 5.1976      |
| 5.5228    | 5.5672     | 5.5415     | 5.5657     | 5.2239      |
| 5.5489    | 5.6969     | 5.5882     | 5.6301     | 5.2955      |
| 5.5900    | 5.7345     | 5.7019     | 5.6947     | 5.3136      |
| 5.6320    | 5.8219     | 5.7097     | 5.7245     | 5.3138      |
| 5.6676    | 5.8625     | 5.8426     | 5.7557     | 5.3908      |
| 5.6782    | 5.9135     | 5.8868     | 5.9183     | 5.4166      |
| 5.7417    | 5.9215     | 5.8877     | 5.9371     | 5.4690      |

| Linker (11) | Linker (12) | Linker (13) |
|-------------|-------------|-------------|
| 3.8015      | 3.5475      | 3.8030      |
| 3.8588      | 3.7465      | 4.1128      |
| 3.8687      | 3.9903      | 4.1577      |
| 4.0057      | 4.2243      | 4.8640      |
| 4.0622      | 4.2920      | 5.2561      |
| 4.1579      | 4.3239      | 5.3900      |
| 4.1943      | 4.5866      | 5.5556      |
| 4.2827      | 4.7326      | 5.7348      |
| 4.4327      | 5.0628      | 5.8707      |
| 4.4539      | 5.1558      | 5.9076      |
| 4.5491      | 5.2436      | 5.9551      |
References

[1] L. Y Liao, X. R Kong, and X. F. Duan. J. Org. Chem., 79:777–782, 2014.

[2] J. M. Veauthier, C. N. Carlson, G. E. Collis, J. L. Kiplinger, and K. D. John. Synthesis (Stuttg.), 2005:2683–2686, 2005.

[3] D. M. D’Souza, D. A. Leigh, M. Papmeyer, and S.L. Woltering. 7, Nat. Protoc.:2022–2028, 2012.

[4] D. C. Harris and M. D. Bertolucci. Symmetry and spectroscopy : an introduction to vibrational and electronic spectroscopy. Oxford University Press, 1978.

[5] S. Zahn, W. Reckien, B. Kirchner, H. Staats, J. Matthey, and A. Lützen. Chem. Eur. J., 15:2572, 2009.

[6] A. Gölle and U. W. Grummt. 321:399–405, 2000.

[7] S. T. Howard. J. Am. Chem. Soc., 118:10269–10274, 1996.

[8] K. Hendrickx, D. E. P. Vanpoucke, K. Leus, K. Lejaeghere, A. Van Yperen-De Deyne, V. Van Speybroeck, P. Van Der Voort, and K. Hemelsoet. Inorg. Chem., 54:10701–10710, 2015.

[9] A. Van Yperen-De Deyne, K. Hendrickx, L. Vanduyfhuys, G. Sastre, P. Van Der Voort, V. Van Speybroeck, and K. Hemelsoet. Theor. Chem. Acc, 135, 2016.