Linear and Nonlinear Optical Properties of Azobenzene Derivatives Modified with (Amino)naphthalene Moiety

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1. SYNTHETIC AND ANALYTICAL GENERAL METHODS

Solvents and starting materials were purchased from commercial suppliers and were used as received. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates (Merck 60F-254). Column chromatography was performed using silica gel (Merck 60, particle size 0.040–0.063 mm). NMR-spectra were recorded on a Bruker AvanceTM 600 MHz spectrometer or on a JEOL 400 MHz spectrometer at 25°C using residual protonated solvent signals as internal standards for $^1$H-and $^{13}$C-spectra. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). High resolution mass spectra (HRMS) were conducted with a WATERS LCT Premier XE mass spectrometer (ESI). High Pressure Liquid Chromatography (HPLC) was done using an Agilent 1260 Infinity II equipped with a chiralpak IB column in hexane/isopropanol.

2. SYNTHESIS AND CHARACTERIZATION

General procedure for azo coupling reaction\(^1\)

Aniline derivative (1equiv) was added into the mixture of H\(_2\)O/EtOH (2/1) and HCl (2 equiv) at 0°C soon afterward dropwise addition of cold water solution of NaNO\(_2\) (1 equiv) over a period of 10 minutes, then the mixture was stirred for 1 h at 0°C. After that time, the reaction mixture was neutralized to pH = 6 using potassium acetate. Next, the diazonium salt solution was added dropwise into the solution of 1-naphthylamine (1equiv) and HCl (1equiv) at H\(_2\)O/EtOH (2:1). The suspension was left stirring for next 1 h at 0°C and left overnight at room temperature. The solution was then neutralized with addition of ammonium solution (25%). Crude product was purified by column chromatography to give the corresponding azobenzene derivative.

General procedure for oxidation of aniline to nitrosoarene derivatives\(^2\)

To a solution of the aniline derivative (1 equiv) in DCM was added the solution of Oxone (2 equiv) in water. The mixture was stirred at room temperature until the reaction was completed (progress of the reaction was monitored by TLC). Then, two phases were separated and the organic phase was washed with water, dried over MgSO\(_4\), filtered, and the solvent was removed under reduced pressure. The resulting nitroso derivatives were used without further purification in the following Mills reaction.
General procedure for Mills reaction

To a solution of the aniline derivative (1 equiv) in acetic acid was added the nitrosoarene (1 equiv) and the resulting mixture was stirred overnight at room temperature. Then the obtained precipitate was filtered and washed thoroughly with water. The resulting solid was purified by column chromatography to give the corresponding azobenzene derivative.

General procedure for reduction of diazonium salts

A solution of amine derivative (1 equiv) and HCl (1 equiv) in H$_2$O/EtOH (2:1) was chilled in an ice-salt bath and treated with cold water solution of sodium nitrate (1 equiv). The resulting solution was stirred for 30 min, and the hypophosphorous acid (50%, 20 equiv) was added dropwise over 10 min. The resulting mixture was left stirring at 0-5°C for 2 h and then left overnight at room temperature. The resulting mixture was neutralized with ammonium solution (25%) and extracted with EtOAc (2x50 mL), washed with water and brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure. The resulting solid was purified by column chromatography to give the corresponding azobenzene derivative (2a, 3a).

Synthesis of 1a-1c

Compound 1b was purchased from Sigma-Aldrich and compound 1c was synthesized according to previously published procedure.

![Scheme S1. Synthetic route for 1a.](#)

Nitrosobenzene: Standard oxidation of aniline to nitrosoarene derivatives procedure was used with aniline (1.20 g, 12.9 mmol) in DCM (40 mL) and Oxone (7.92 g, 25.8 mmol) in H$_2$O (120 mL) to give nitrosobenzene as brown crystals that was used as such in the next step.

1a: Standard Mills reaction procedure was used with nitrosobenzene (1.38 g, 12.9 mmol) and aniline (1.20 g, 12.9 mmol) in AcOH (70 mL). The residue was purified by column
chromatography using as eluent pure hexanes to DCM/hexanes 30/70 to yield 1 (1.34 g, 57%) as an orange solid. \textbf{1H NMR} (601 MHz, Chloroform-d) \(\delta\): 7.95 – 7.92 (m, 4H), 7.55 – 7.51 (m, 4H), 7.50 – 7.45 (m, 2H). \textbf{HRMS} m/z (ESI): C\textsubscript{12}H\textsubscript{10}N\textsubscript{2} [M+H]\textsuperscript{+}, calculated: 183.0922, found: 183.0917.

\textbf{Figure S1.} \textsuperscript{1}H NMR spectrum of 1a.
Synthesis of 2a-2c

Scheme S2. Synthetic route for 2a and 2b

2b: Standard azo coupling procedure was used with aniline (3.0 g, 32.2 mmol) in H₂O/EtOH (20/10 mL), HCl (10 M, 6.4 mL), NaNO₂ (2.2 g, 32.2 mmol) and then 1-naphtylamine (4.6 g, 32.2 mmol) in H₂O/EtOH (75/25 mL), HCl (10 M, 3.2 mL). The residue was purified by column chromatography using as eluent hexanes/CH₂Cl₂ 1/1 to pure CH₂Cl₂ to yield 2b (4.8 g, 60%) as a red solid. ¹H NMR (601 MHz, Methylene Chloride-d₂) δ: 9.11 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 7.7 Hz, 2H), 7.98 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.61 – 7.54 (m, 3H), 7.48 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 4.70 (s, 2H). ¹³C NMR (151 MHz, Methylene Chloride-d2) δ: 153.6, 146.8, 140.0, 133.2, 129.8, 129.1, 127.2, 125.3, 123.9, 122.6, 122.4, 120.8, 114.0, 108.9. HRMS m/z (ESI): C₁₆H₁₃N₃ [M+H]^+, calculated: 248.1188, found: 248.1186.
Figure S2. $^1$H NMR spectrum of 2b.

Figure S3. $^{13}$C NMR spectrum of 2b.
2a: Standard reduction of diazonium salts procedure was used with 2b (0.3 g, 1.21 mmol) in 
H₂O/EtOH (8/4 mL), HCl (10 M, 1.2 mL), NaNO₂ (83.5 mg, 1.21 mmol) and H₃PO₄ (50%, 
1.07 mL). The residue was purified by column chromatography using as eluent pure hexanes to 
hexanes/CH₂Cl₂ 90/10 to yield 2a (165 mg, 59%) as a red solid. ¹H NMR (601 MHz, Methylene 
Chloride-d₂) δ: 8.94 (d, J = 8.4, 1.1 Hz, 1H), 8.08 – 8.04 (m, 2H), 8.03 (d, J = 8.1 Hz, 1H), 7.97 
(d, J = 8.2 Hz, 1H), 7.84 (dd, J = 7.5, 1.1 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.64 – 7.56 (m, 4H), 
7.57 – 7.51 (m, 1H). ¹³C NMR (151 MHz, Chloroform-d) δ 153.2, 147.8, 134.4, 131.4, 131.1, 
129.2, 128.0, 126.9, 126.5, 125.7, 123.5, 123.2, 111.9. HRMS m/z (ESI): C₁₆H₁₂N₂ [M+H]+, 
calculated: 233.1079, found: 233.1077.

Figure S4. ¹H NMR spectrum of 2a.
Figure S5. $^{13}$C NMR spectrum of 2a.

Scheme S3. Synthetic route for 2c.

2: Standard azo coupling procedure was used with 4-nitroaniline (1.38 g, 10 mmol) in H$_2$O/EtOH (20/10 mL), HCl (10 M, 2.0 mL), NaNO$_2$ (0.69 g, 10 mmol) and then 1-naphtylamine (1.43 g, 10 mmol) in H$_2$O/EtOH (20/10 mL), HCl (10 M, 1.0 mL). The residue was purified by column chromatography using as eluent pure hexanes to hexanes/CH$_2$Cl$_2$ 50/50 to yield 2 (0.94 g, 32%) as a purple solid. $^1$H NMR (400 MHz, Methylene Chloride-$d_2$) $\delta$: 9.05 (d, $J = 8.0$ Hz, 1H), 8.42 – 8.30 (m, 2H), 8.10 – 8.03 (m, 3H), 7.87 (d, $J = 8.5$ Hz, 1H), 7.74 –
7.67 (m, 1H), 7.64 – 7.54 (m, 1H), 6.86 (d, J = 8.5 Hz, 1H), 4.98 (br s, 2H). **HRMS** m/z (ESI): C_{16}H_{12}N_{4}O_{2} [M+H]^+, calculated: 293.1039, found: 293.1043.

**2c:** To a solution of **2** (0.16 g, 0.55 mmol, 1 equiv) in H$_2$O/THF 1:3 v/v (40 mL), Na$_2$S (0.396 g, 1.65 mmol, 3 equiv) was added and the mixture was refluxed for 4 h. The THF was evaporated and residues were diluted with 1 M NaOH and extracted with EtOAc (3 x 50 mL). Layers were separated and organic layers were combined, washed with brine and dried over MgSO$_4$. After evaporation of the solvent, crude product was purified by column chromatography on SiO$_2$ gradient from CHCl$_3$ to 99/2 CHCl$_3$/MeOH to give product as deep red powder (0.12 g, 82%).

**$^1$H NMR** (400 MHz, Methylene Chloride-$d_2$) δ: 9.00 (d, J = 8.4 Hz, 1H), 7.89 – 7.78 (m, 4H), 7.66 – 7.60 (m, 1H), 7.58 – 7.51 (m, 1H), 6.83 (d, J = 8.3 Hz, 1H), 6.81 – 6.74 (m, 2H), 4.60 (s, 2H), 4.08 (s, 2H). **$^{13}$C NMR** (151 MHz, Methylene Chloride-$d_2$) δ: 149.0, 146.3, 145.3, 140.3, 132.7, 126.6, 125.1, 124.5, 124.0, 122.6, 120.7, 114.6, 113.1, 109.1. **HRMS** m/z (ESI): C$_{16}$H$_{14}$N$_4$ [M+H]^+, calculated: 263.1297, found: 263.1295.

![Figure S6. $^1$H NMR spectrum of 2c.](image-url)
**Synthesis of 3a-3c**

3b: Standard azo coupling procedure was used with 4-aminazobenzene (1.97 g, 10 mmol) in H$_2$O/EtOH (30/15 mL), HCl (10 M, 2 mL), NaNO$_2$ (0.69 g, 10 mmol) and then 1-naphtylamine (1.43 g, 10 mmol) in H$_2$O/EtOH (20/10 mL), HCl (10 M, 1.0 mL). The residue
was purified by column chromatography using as eluent pure hexanes to hexanes/CH₂Cl₂ 50/50 to yield 3b (2.53 g, 72%) as dark purple solid. \textbf{1H NMR} (601 MHz, Methylene Chloride-\textit{d}₂) δ: 9.10 (d, \( J = 8.5 \) Hz, 1H), 8.15 – 8.12 (m, 2H), 8.12 – 8.09 (m, 2H), 8.02 (d, \( J = 8.3 \) Hz, 1H), 8.00 – 7.97 (m, 2H), 7.85 (d, \( J = 8.4 \) Hz, 1H), 7.73 – 7.67 (m, 1H), 7.61 – 7.46 (m, 4H), 6.84 (d, \( J = 8.3 \) Hz, 1H), 4.82 (s, 2H). \textbf{13C NMR} (151 MHz, Methylene Chloride-d₂) δ: 155.5, 153.4, 153.4, 148.0, 140.8, 134.0, 131.8, 129.7, 128.0, 126.0, 124.4, 124.4, 124.0, 123.5, 122.8, 121.3, 115.00, 109.5. \textbf{HRMS} m/z (ESI): C_{22}H_{17}N₅ [M+H]^+, calculated: 352.1562, found: 352.1563.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure_S8}
\caption{\textbf{1H NMR} spectrum of 3b.}
\end{figure}
3a: Standard reduction of diazonium salts procedure was used with 3b (0.17 g, 0.48 mmol) in H₂O/EtOH (4/2 mL), HCl (10 M, 0.96 mL), NaNO₂ (33 mg, 0.48 mmol) and H₃PO₄ (50%, 0.43 mL). The residue was purified by column chromatography using as eluent pure hexanes to hexanes/CH₂Cl₂ 70/30 to yield 3a (108 mg, 67%) as a red/orange solid. **¹H NMR** (400 MHz, Methylene Chloride-d₂) δ: 8.99 (d, J = 8.4 Hz, 1H), 8.22 – 8.20 (m, 2H), 8.15 – 8.12 (m, 2H), 8.06 (d, J = 8.1 Hz, 1H), 8.04 – 7.94 (m, 3H), 7.91 (d, J = 7.5 Hz, 1H), 7.77 – 7.66 (m, 1H), 7.68 – 7.49 (m, 5H). **¹³C NMR** (151 MHz, Methylene Chloride-d₂) δ 154.8, 154.3, 153.3, 148.3, 135.0, 132.5, 132.1, 132.0, 129.8, 128.6, 127.7, 127.2, 126.2, 124.6, 124.4, 123.9, 123.6, 112.5. **HRMS** m/z (ESI): C₂₂H₁₆N₄ [M+H]^+, calculated: 337.1453, found: 337.1453.
Figure S10. $^1$H NMR spectrum of 3a.

Figure S11. $^{13}$C NMR spectrum of 3a.
**Scheme S5. Synthetic route for 3c.**

5: Standard oxidation of aniline to nitrosoarene derivatives procedures was used with 4-nitroaniline (1.45 g, 10.5 mmol) in DCM (25 mL) and Oxone (6.17 g, 20.1 mmol) in H₂O (75 mL) to give 5 as a deep green liquid that was used as such in the next step.

6: Standard Mills reaction procedure was used with 5 (1.6 g, 10.5 mmol) and 4-aminoacetanilide (1.58 g, 10.5 mmol) in AcOH (70 mL). The residue was purified by column chromatography using as eluent pure DCM to DCM/MeOH 97/3 to yield 6 (2.3 g, 77%) as a red solid. **¹H NMR** (400 MHz, Acetone-d₆) δ: 9.57 (s, 1H), 8.51 – 8.38 (m, 2H), 8.16 – 8.03 (m, 2H), 8.01 – 7.94 (m, 2H), 7.93 – 7.85 (m, 2H), 2.15 (s, 3H). **HRMS** m/z (ESI): C₁₄H₁₂N₄O₃ [M+H]+, calculated: 285.0988, found: 285.0986.

3: To a solution of 6 (0.83 g, 2.9 mmol, 1 equiv) in H₂O/THF 1:3 v/v (90 mL), Na₂S (2.1 g, 8.7 mmol, 3 equiv) was added and the mixture was refluxed for 7 h. The THF was evaporated and residues were diluted with 1 M NaOH and extracted with EtOAc (3x50 mL). Layers were separated and organic layers were combined, washed with brine and dried over MgSO₄. After evaporation of the solvent, crude product was purified by column chromatography on SiO₂ gradient from DCM to 98/2 DCM/MeOH to give product as an orange powder (0.51 g, 69%). **¹H NMR** (601 MHz, DMSO-d₆) δ: 10.23 (s, 1H), 7.70 – 7.66 (m, 2H), 7.65 – 7.57 (m, 4H), 6.68 – 6.64 (m, 2H), 5.78 (s, 2H), 2.05 (s, 3H). **HRMS** m/z (ESI): C₁₄H₁₄N₄O [M+H]+, calculated: 255.1246, found: 255.1254.
4. Aniline derivative (3) (0.25 g, 0.98 mmol, 1 equiv) was added into the mixture of H₂O/EtOH (10/5) and HBF₄ (48% in H₂O, 0.33 mL, 2.6 equiv) at 0°C. Then cold water (1 mL) solution of NaNO₂ (68 mg, 0.98 mmol, 1 equiv) was added over a period of 10 minutes and the mixture was stirred for 1 h at 0°C. Next, the diazonium salt solution was added dropwise into the solution of 1-naphthylamine (140 mg, 0.98 mmol, 1 equiv) and HCl (10 M, 98 μL) at H₂O/EtOH (10/5 mL). The mixture was stirred for 1 h at 0°C and then left overnight at room temperature. The ethanol was evaporated and mixture basified with ammonium solution and extracted with DCM. Layers were separated and organic layers were combined, washed with brine and dried over MgSO₄. After evaporation of the solvent, crude product was purified by column chromatography on SiO₂ gradient from DCM to DCM/MeOH 97/3 to give 4 as a deep purple powder (72 mg, 18%).

1H NMR (601 MHz, Methanol-d4) δ: 9.02 – 9.00 (m, 1H), 8.11 – 8.03 (m, 5H), 7.99 (d, J = 8.5 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.81 – 7.76 (m, 2H), 7.66 – 7.61 (m, 1H), 7.54 – 7.49 (m, 1H), 6.83 (d, J = 8.5 Hz, 1H), 2.18 (s, 3H).

13C NMR (151 MHz, Methanol-d4) δ: 171.9, 156.4, 154.0, 151.8, 150.3, 143.1, 140.1, 135.3, 128.5, 125.9, 124.9, 124.7, 124.4, 123.3, 123.0, 121.1, 116.3, 109.2. HRMS m/z (ESI): C₂₄H₂₀N₆O [M+H]⁺, calculated: 409.1777, found: 409.1768.

3c: To a solution of 4 (30 mg, 7.3 mmol, 1 equiv) in methanol (6 mL), 1 mL of 6 M HCl was added and heated at 75°C for 8 h. Methanol was evaporated and the mixture was basified with 1 M NaOH and extracted with DCM (3x20 mL). Layers were separated and organic layers were combined, washed with brine and dried over MgSO₄. After evaporation of the solvent, crude product was purified by column chromatography on SiO₂ gradient from DCM to DCM/MeOH 98/2 to give product as a deep purple powder (20 mg, 75%).

1H NMR (400 MHz, Methylene Chloride-d2) δ: 9.09 (d, J = 7.9 Hz, 1H), 8.12 – 8.06 (m, 2H), 8.03 – 7.96 (m, 3H), 7.89 – 7.81 (m, 3H), 7.73 – 7.65 (m, 1H), 7.62 – 7.55 (m, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.80 – 6.75 (m, 2H), 4.81 (s, 1H), 4.22 (s, 1H).

13C NMR (101 MHz, Methylene Chloride-d2) δ: 154.1, 153.4, 150.4, 147.2, 145.6, 140.3, 133.4, 127.4, 125.4, 125.3, 123.9, 123.4, 123.2, 122.3, 120.8, 114.5, 114.2, 109.0. HRMS m/z (ESI): C₂₂H₁₈N₆[M+H]⁺, calculated: 367.1671, found: 367.1667.
Figure S12. $^1$H NMR spectrum of 3c.

Figure S13. $^{13}$C NMR spectrum of 3c.
3. PHOTOISOMERIZATION STUDIES

**Figure S14.** Transmittance spectra of the filters used for irradiation.

**Figure S15.** Chromatograms of 1a after irradiation with 313 nm and then 436 nm, the composition of PSS$_{313}$ nm found to be 80/20% of Z/E and that at PSS$_{436}$ nm found to be 15/85% Z/E.
4. THERMAL STABILITY

Figure S16. Thermal 1a-Z to 1a-E isomerization in acetonitrile at four temperatures 50°C, 55°C, 60°C, 65°C. Red lines represent the data fitting curve (first-order kinetics).

Figure S17. Thermal 2a-Z to 2a-E isomerization in acetonitrile at four temperatures 50°C, 55°C, 60°C, 65°C. Red lines represent the data fitting curve (first-order kinetics).
Figure S18. Thermal 3a-Z to 3a-E isomerization in acetonitrile at four temperatures 20°C, 30°C, 35°C, 40°C. Red lines represent the data fitting curve (first-order kinetics).

Figure S19. Arrhenius plots for 1a, 2a and 3a in acetonitrile, rate constants of the Z-E isomerization process at different temperatures were determined by the exponential curve fitting of the plot: absorbance vs. time. The slope is equal to -E_a/R.
Figure S20. Eyring plots for 1a, 2a and 3a in acetonitrile, the slope is equal to $-\Delta H^\ddagger / R$, intercept: $\ln((k_{A_b})/h) + \Delta S^\ddagger / R$.

Table S1. Isomerization rates $k_{Z\to E}$ (at 298 K), thermal half-life $\tau_{1/2}$ (at 298 K), Arrhenius prefactor $A$, activation energies $E_a$, as well as Eyring activation free energies $\Delta G^\ddagger$, enthalpies $\Delta H^\ddagger$ and entropies $\Delta S^\ddagger$ for compounds 1a, 2a and 3a in acetonitrile.

| Cmpd | $k_{E\to Z}^{[a]}$ [s$^{-1}$] | $\ln k_{E\to Z}$ | $\tau_{1/2}$ [h] | $A^{[c]}$ [s$^{-1}$] | $E_a$ [kJ mol$^{-1}$] | $\Delta H^\ddagger$ [kJ mol$^{-1}$] | $\Delta S^\ddagger$ [J mol$^{-1}$ K$^{-1}$] | $\Delta G^\ddagger$ [kJ mol$^{-1}$] |
|------|----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1a   | 6.0 ± 2.9                  | -14.3 ± 0.7     | 322 ± 155       | 7.6 ± 3.4       | 103.3 ± 1.6     | 100.6 ± 1.6     | 26.6 ± 4.9       | 108.5 ± 2.2     |
| 2a   | 209 ± 110                  | -10.8 ± 0.7     | 9.2 ± 4.8       | 3.3 ± 1.6       | 92.4 ± 1.8      | 89.7 ± 1.8      | 33.6 ± 5.4       | 99.7 ± 2.4      |
| 3a   | 3760 ± 2400                | -7.9 ± 1.0      | 0.51 ± 0.30     | 14.4 ± 8.9      | 88.9 ± 2.5      | 86.3 ± 2.5      | 20.6 ± 8.1       | 92.5 ± 3.5      |

[a] $10^{-7}$ at 298 K. [b] estimated from Arrhenius equation at 298 K. [c] $10^{11}$
5. Z-SCAN STUDIES

Figure S21. Representative Z-scan traces of 1c at 750 nm: left closed-aperture (CA) (black squares); right open-aperture (OA) (black squares). The red curves correspond to the theoretical curves.

Figure S22. Overlay of one and two-photon absorption spectra for 1b (left) and 1c (right) in DMSO at 20 °C.
6. THEORETICAL CALCULATIONS

Figure S23. Atom numbering.
Figure S24. NBO partial atomic charges estimated within the \omega B97X-D/def2-TZVP/PCM(DMSO) approach.
Figure S25. Electrostatic potential for 1a-3c for optimized structures.
The pyramidalization of the amino group is a natural feature of the amino-compounds, explained by their tendency to adopting of the sp$^3$ hybridization at nitrogen. The pyramidalization angle for the amino groups in the analyzed systems is presented in the table below with the dihedral angles H-N-C-H as its measure (-180 degrees would correspond to the planar -NH$_2$ group):

**Table S2.** The pyramidalization angle for the amino groups of the investigated compounds.

| Dihedral angle [degrees] | wB97X-D/def2-TZVP/PCM(DCM) |
|--------------------------|------------------------------|
|                          | H24-N9-C4-H25 | H27-N22-C17-H28 |
| 1b- E                    | -142.06       |                |
| 1c- E                    | -138.60       | -138.60        |
| 2b- E                    | -142.46       |                |
| 2c- E                    | -137.96       | -137.40        |
| 3b- E                    | -145.95       |                |
| 3c- E                    | -144.30       | -142.48        |

It can be clearly noticed that the amino-group is not planar, the nitrogen is slightly (about 3 degrees) pushed below the surface, but the hydrogens significantly deviate from planarity (C-C-N-H dihedrals all about 20 degrees). Thus, it will break the planar symmetry of the C$_{2h}$ point group observed for the ideal unsubstituted azobenzene 1a, and in the case of 1c lead to C$_{1}$-like symmetry, with the pyramidalization of both groups in opposite directions. The growing size of the analyzed azobenzene molecules additionally results in the asymmetric pyramidalization of both amino groups present in the system. Namely, for 1c both amino groups are characterized with the same dihedral angle (Table S2) equal to -138.6 degrees. For 2c, the small difference of these two dihedrals appears and it gets more pronounced for 3c (-144.30 versus -142.48 degrees). This introduces further deviation from the C$_{2h}$-like symmetry point group.
Figure S26. Normalized experimental and calculated UV-Vis spectra of 1a-1c in DMSO.

Figure S27. Normalized experimental and calculated UV-Vis spectra of 2a-2c in DMSO.
Figure S28. Normalized experimental and calculated UV-Vis spectra of 3a-3c in DMSO.
Figure S29. Vertical absorption spectrum estimated in B97X-D/def2/TZVP/PCM(DMSO) approach together with the most important natural transition orbitals for 1a, 1b and 1c systems.
Figure S30. Vertical absorption spectrum estimated in ωB97X-D/def2/TZVP/PCM(DMSO) approach together with the most important natural transition orbitals for 2a, 2b and 3a systems.
Table S3. Second-order perturbation theory analysis of the Fock matrices in NBO basis for systems containing one and two amino groups: LP denotes the lone pair at the corresponding nitrogen of the NH₂ group, the BD* stands for the antibonding orbital in the aromatic ring. E(2) describes the stabilization arising from the donor-acceptor interaction, E(j) and E(i) are the acceptor and donor orbital energies, respectively and F(i,j) are the resonance integrals of the real-world one electron effective Hamiltonian. Data presented for E isomer.

| Donor NBO (i) | Acceptor NBO (j) | E(2) (kcal/mol) | E(j)-E(i) (a.u.) | F(i,j) (a.u.) |
|---------------|-----------------|----------------|----------------|------------|
| NH₂ at the phenyl/naphthalene ring |
| 1b | LP N9 | BD* C4-C5 | 48.37 | 0.42 | 0.134 |
| 2b | LP N22 | BD* C16-C17 | 53.48 | 0.43 | 0.140 |
| 3b | LP N22 | BD* C16-C17 | 57.83 | 0.42 | 0.144 |
| NH₂ at the terminal phenyl ring |
| 1c | LP N9 | BD* C4-C5 | 44.39 | 0.43 | 0.131 |
| 2c | LP N9 | BD* C4-C5 | 43.01 | 0.43 | 0.129 |
| 3c | LP N42 | BD* C36-C37 | 48.97 | 0.42 | 0.135 |
| NH₂ at the phenyl/naphthalene ring |
| 1c | LP N22 | BD* C16-C17 | 44.39 | 0.43 | 0.131 |
| 2c | LP N22 | BD* C16-C17 | 47.30 | 0.44 | 0.134 |
| 3c | LP N22 | BD* C16-C17 | 55.75 | 0.42 | 0.142 |

Table S4. Relative energy, relative Gibbs free energy and the molar fraction of the Z₁Z₂, Z₁E₂, E₁Z₂ and E₁E₂ isomers of 3a in the mixture in standard conditions (ωB97X-D/def2/TZVP/PCM(DMSO))

| | Relative energy (kcal/mol) | Relative Gibbs free energy, (kcal/mol) | Molar fraction |
|-----------------|-----------------|-----------------|-------------|
| Z₁Z₂            | 15.41           | 18.18           | 0.9999      |
| Z₁E₂            | 9.86            | 11.20           | 0.0000      |
| E₁Z₂            | 7.13            | 8.54            | 0.0000      |
| E₁E₂            | 0.00            | 0.00            | 0.0000      |
Table S5. Ground (GS) and excited (ES) states dipole moments calculated using ωB97X-D/def2-TZVP/PCM(DMSO) level of theory.

| Compound | μ<sup>GS</sup> (D) | λ<sub>1PA</sub> (nm) | μ<sup>ES</sup> (D) |
|----------|------------------|------------------|------------------|
| 1a       |                  |                  |                  |
| E        | 0.00             | 310              | 0.00             |
| Z        | 4.27             | 433              | 3.83             |
| 1b       | 3.95             | 349              | 10.25            |
| 1c       | 0.00             | 365              | 0.00             |
| 2a       |                  |                  |                  |
| E        | 0.23             | 328              | 4.35             |
| Z        | 4.37             | 437              | 4.31             |
| 2b       | 5.01             | 378              | 9.33             |
| 2c       | 0.80             | 386              | 1.04             |
| 3a       |                  |                  |                  |
| E<sub>1</sub>E<sub>2</sub> | 0.28             | 361              | 2.83             |
| E<sub>1</sub>Z<sub>2</sub> | 4.25             | 323              | 4.60             |
| Z<sub>1</sub>E<sub>2</sub> | 4.51             | 338              | 7.22             |
| Z<sub>1</sub>Z<sub>2</sub> | 4.62             | 283              | 3.79             |
| 3b       | 6.11             | 417              | 7.32             |
| 3c       | 2.49             | 424              | 3.27             |

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Figure S31. Overlay of 1PA and 2PA for 2a-c, calculated with the CAM-B3LYP/def2-TZVP/PCM(DMSO) (upper panel) and experimentally found (lower panel) in DMSO at 20 °C.

Figure S32. Overlay of 1PA and 2PA for 3a-c, calculated with the CAM-B3LYP/def2-TZVP/PCM(DMSO) (upper panel) and experimentally found (lower panel) in DMSO at 20 °C.
Figure S33. Frontier molecular orbitals involved in the most intensive 1PA and 2PA transitions and their symmetry for the C\(_{2h}\)-like point group.
**Figure S34.** Schematic presentation of the states for 1c, 2c and 3c with 1PA and 2PA symmetry-allowed and symmetry-forbidden transitions.

**Table S6.** Symmetry assignment for the frontier orbitals in the C$_{2h}$-like point group for 2c and 3c

| 2c orbital | E | C$_2$ | i | $\sigma_h$ | Representation |
|------------|---|-------|---|------------|----------------|
| HOMO       | 1 | 1     | -1| -1         | a$_u$-like     |
| LUMO       | 1 | -1    | 1 | -1         | b$_g$-like     |
| LUMO+1     | 1 | -1    | 1 | -1         | b$_g$-like     |

| 3c orbital | E | C$_2$ | i | $\sigma_h$ | Representation |
|------------|---|-------|---|------------|----------------|
| HOMO-1     | 1 | 1     | -1| -1         | a$_u$-like     |
| HOMO       | 1 | -1    | 1 | -1         | b$_g$-like     |
| LUMO       | 1 | 1     | -1| -1         | a$_u$-like     |
Table S7. Oscillator strength corresponding to the intensity of the 1PA signals, 2PA cross sections, transition character, numbers of involved frontier orbitals and symmetry of the transition for 1c(E), 2c(E) and 3c(EE); last two columns contain the indication of the forbidden (F) or allowed (A) transition according to the parity considerations based on Laporte rule

|       | 1PA 2PA | 1PA 2PA | 1PA 2PA | 1c(E) | 1PA 2PA |
|-------|---------|---------|---------|-------|---------|
|       | 1a(E)   | 1b(E)   |         |       |         |
| S0→S1 | 0.00    | 0       | 0.00    | 0     | n->π⁺  |
|       | 54->57  | a₂g x   |         | b₂g   | F       |
| S0→S2 | 0.92    | 1.05    | 115     | 1.20  | π->π⁺  |
|       | 56->57  | a₂x b₂u |         | b₂u   | A       |
| S0→S3 | 0.05    | 0.02    | 4       | 0.00  | 1946    |
|       | 146     | a₂u a₂x |         | a₂x   | F       |
|       |         |         |         |       |         |
|       | 2a(E)   | 2b(E)   |         |       | 2c(E)   |
| S0→S1 | 0.05    | 2       | 0.03    | 1     | n->π⁺  |
|       | 67->70  | a₂g x   |         | b₂g   | F       |
| S0→S2 | 0.62    | 33      | 0.95    | 59    | π->π⁺  |
|       | 69->70  | a₂u b₂u |         | a₂u   | A       |
| S0→S3 | 0.01    | 7       | 0.02    | 10    | π->π⁺  |
|       | 69->71  | a₂u b₂u |         | a₂u   | A       |
|       |         |         |         |       |         |
|       | 3a(EE)  | 3b(EE)  |         |       | 3c(EE)  |
| S0→S1 | 0.14    | 16      | 0.11    | 76    | n->π⁺  |
|       | 94->97  | a₂g x   |         | a₂u   | A       |
| S0→S2 | 0.00    | 0       | 0.01    | 10    | n->π⁺  |
|       | 95->97  | a₂u a₂x |         | a₂x   | F       |
| S0→S3 | 1.45    | 51      | 1.60    | 1.60  | π->π⁺  |
|       | 96->97  | b₂g x   |         | b₂u   | A       |
| S0→S4 | 0.14    | 607     | 0.15    | 0.15  | π->π⁺  |
|       | 95->97  | a₂u a₂x |         | a₂x   | F       |

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