Electronic Supplementary Information

Simple 1-dicyanomethylene-2-chloro-3-aminoundene push-pull chromophores: applications in cation and anion sensing

Sara Basurto, Daniel Miguel, Daniel Moreno, Ana G. Neo, Roberto Quesada, Tomás Torroba

a Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Plaza Misael Bañuelos s/n, 09001 Burgos, Spain. Fax: 34 947 258831; Tel: 34 947 258088; E-mail: ttorroba@ubu.es
b Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain. Fax: 34 983 423234; Tel: 34 983 184096; E-mail: dmsj@qi.uva.es
c Departamento de Química Orgánica, Facultad de Veterinaria, Universidad de Extremadura, Avenida de la Universidad s/n, 10071 Cáceres, Spain. Fax: 34 927 257110; Tel: 34 927 257158; E-mail: aneo@unex.es

Contents:

1. Crystal Structure determination for compound 3
2. NMR and UV spectra of compounds 2-10
3. Titration Materials and Methods
4. Colorimetric Studies
5. Reversibility studies
6. \(^1\)H NMR Titration Studies
7. Kinetic studies
1. Crystal Structure determination for compound 3

A single crystal of 3 was mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å).\(^{1a}\) Intensities were integrated\(^{1b}\) from several series of exposures, each exposure covering 0.3° in $\omega$, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.\(^{1c}\) The structure was solved by direct methods and refined by least squares on weighted $F^2$ values for all reflections.\(^{1d}\) All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals. Complex neutral-atom scattering factors were used.\(^{1e}\)

Table 1. Crystal data and structure refinement for 3.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>neo163am</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C20 H22 Cl N3</td>
</tr>
<tr>
<td>Formula weight</td>
<td>339.86</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
</tbody>
</table>
| Unit cell dimensions  | a = 8.3304(16) Å, $\alpha = 92.955(4)^{\circ}$.
|                       | b = 9.1897(18) Å, $\beta = 97.382(4)^{\circ}$.
|                       | c = 13.096(3) Å, $\gamma = 108.536(4)^{\circ}$.
| Volume                | 938.1(3) Å$^3$            |
| Z                     | 2                         |
| Density (calculated)  | 1.203 Mg/m$^3$            |
| Absorption coefficient| 0.209 mm$^{-1}$           |
| F(000)                | 360                       |
| Crystal size          | 0.31 x 0.13 x 0.09 mm$^3$ |
| Theta range for data collection | 1.58 to 23.33$^{\circ}$. |
| Index ranges          | -9$\leq$h$\leq$9, -10$\leq$k$\leq$8, -14$\leq$l$\leq$12 |
| Reflections collected | 4227                      |
| Independent reflections| 2673 [R(int) = 0.0248]     |
| Completeness to theta = 23.33$^{\circ}$ | 98.3 %                   |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000000 and 0.627933      |
Refinement method
Full-matrix least-squares on F^2

Data / restraints / parameters
2673 / 0 / 221

Goodness-of-fit on F^2
1.038

Final R indices [I>2sigma(I)]
R1 = 0.0635, wR2 = 0.1733

R indices (all data)
R1 = 0.0874, wR2 = 0.1891

Largest diff. peak and hole
0.477 and -0.403 e.Å^-3


**Fig. 1.** Crystal packing of 3
2. NMR and UV spectra of compounds 2-10.

Fig. 2. $^1$H NMR (CDCl$_3$, 400 MHz) of 2
Fig. 3. $^{13}$C NMR (CDCl$_3$, 75 MHz) of 2

2.5$x10^{-5}$M, CH$_3$CN

Fig. 4. UV-vis (CH$_3$CN, 2.5$x10^{-5}$ M) of 2
Fig. 5. $^1$H NMR (CDCl$_3$, 400 MHz) of 3

Fig. 6. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 3
Fig. 7. $^1$H NMR (CDCl$_3$, 400 MHz) of 4

Fig. 8. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 4
Fig. 9. UV-vis (CH$_3$CN, 10$^{-4}$ M) of 4

Fig. 10. $^1$H NMR (CDCl$_3$, 400 MHz) of 5
Fig. 11. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 5

Fig. 12. UV-vis (CH$_2$Cl$_2$, 2.5x10$^{-5}$ M) of 5
Fig. 13. $^1$H NMR (CDCl$_3$, 400 MHz) of 6

Fig. 14. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 6
Fig. 15. UV-vis (CH₂Cl₂, 2.5x10⁻⁵ M) of 6

Fig. 16. ¹H NMR (CDCl₃, 400 MHz) of 7
Fig. 17. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 7

Fig. 18. UV-vis (CH$_2$Cl$_2$, 2.5x10$^{-5}$ M) of 7
Fig. 19. $^1$H NMR (CDCl$_3$, 400 MHz) of 8

Fig. 20. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 8
Fig. 21. UV-vis (CH₂Cl₂, 2.5x10⁻⁵ M) of 8

Fig. 22. ¹H NMR (CDCl₃, 400 MHz) of 9
Fig. 23. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 9

Fig. 24. UV-vis (CH$_3$CN, $10^{-4}$ M) of 9
Fig. 25. $^1$H NMR (CDCl$_3$, 400 MHz) of 10

Fig. 26. $^{13}$C NMR (CDCl$_3$, 100 MHz) of 10
Fig. 27. DEPT NMR (CDCl₃, 100 MHz) of 10

2.5*10⁻⁵ M, CH₃CN

Fig. 28. UV-vis (CH₃CN, 2.5x10⁻⁵ M) of 10
3. Titration Materials and Methods.

Perchlorate salts were used for some cations and triflate salts for the rest of cations:

<table>
<thead>
<tr>
<th>CATION</th>
<th>SALT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>AgClO₄ · xH₂O</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Ni(ClO₄)₂ · 6H₂O</td>
</tr>
<tr>
<td>Sn²⁺</td>
<td>Sn(CF₃SO₃)₂</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Cd(ClO₄)₂</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Zn(CF₃SO₃)₂</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Pb(ClO₄)₂</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Cu(ClO₄)₂ · 6H₂O</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Fe(ClO₄)₃ · xH₂O</td>
</tr>
<tr>
<td>Sc³⁺</td>
<td>Sc(CF₃SO₃)₃</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>Al(ClO₄)₃ · 9H₂O</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Hg(ClO₄)₂</td>
</tr>
</tbody>
</table>

5×10⁻² M, 5×10⁻³ M, 5×10⁻⁴ M solutions of every salt were prepared, then a 10⁻⁴ M solution of the compound under study was prepared. For qualitative experiments, 2 mL solution of the compound under study were measured and the corresponding amount of salt was added by micropipette.

Eppendorf Research micropipette characteristics:

<table>
<thead>
<tr>
<th>MODEL</th>
<th>Ep T.I.P.S.</th>
<th>Volume</th>
<th>Systematic error of measurement</th>
<th>Random error of measurement (CV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 - 20μL</td>
<td>2 - 200</td>
<td>2 μL</td>
<td>± 5.0 %</td>
<td>≤ 1.5 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 μL</td>
<td>± 1.2 %</td>
<td>≤ 0.6 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 μL</td>
<td>± 1.0 %</td>
<td>≤ 0.3 %</td>
</tr>
<tr>
<td>10 - 100μL</td>
<td>2 - 200</td>
<td>10 μL</td>
<td>± 3.0 %</td>
<td>≤ 1.0 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 μL</td>
<td>± 1.0 %</td>
<td>≤ 0.3 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 L</td>
<td>± 0.8 %</td>
<td>≤ 0.2 %</td>
</tr>
<tr>
<td>100 - 1000μL</td>
<td>50 - 1000</td>
<td>100 μL</td>
<td>± 3.0 %</td>
<td>≤ 0.6 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5000 μL</td>
<td>± 1.0 %</td>
<td>≤ 0.2 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000 μL</td>
<td>± 0.6 %</td>
<td>≤ 0.2 %</td>
</tr>
<tr>
<td>500 - 5000μL</td>
<td>100 - 5000</td>
<td>500 μL</td>
<td>± 2.4 %</td>
<td>≤ 0.6 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500 μL</td>
<td>± 1.2 %</td>
<td>≤ 0.25 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5000 μL</td>
<td>± 0.6 %</td>
<td>≤ 0.15 %</td>
</tr>
</tbody>
</table>
4. Colorimetric studies

Fig. 29. UV titration of 2 (10^{-4} M, CH_{3}CN) with Sc^{3+}

Fig. 30. Titration profile of 2 (10^{-4} M, CH_{3}CN) and Sc^{3+}, \lambda=550nm

Fig. 31. UV titration of 2 (10^{-4} M, CH_{3}CN) with Sn^{2+}
**Fig. 32.** Titration profile of 2 (10^{-4} M, CH_{3}CN), with Sn^{2+}, \lambda=550\text{nm}

**Fig. 33.** UV titration of 2 (10^{-4} M, CH_{3}CN), with Al^{3+}.

**Fig. 34.** Titration profile of 2 (10^{-4} M, CH_{3}CN), and Al^{3+}, \lambda=550\text{nm}
**Fig. 35.** UV titration of $2$ ($10^{-4}$ M, CH$_3$CN) with Fe$^{3+}$.

**Fig. 36.** Titration profile of $2$ ($10^{-4}$ M, CH$_3$CN) with Fe$^{3+}$ at $\lambda=550$ nm.

**Fig. 37.** UV titration of $2$ ($10^{-4}$ M, CH$_3$CN) with Cu$^{2+}$.
**Fig. 38.** Titration profile of 2 (10^{-4} M, CH₃CN) with Cu²⁺

**Fig. 39.** UV titration of 4 (10^{-4} M, CH₃CN) with Cu²⁺

**Fig. 40.** Titration profile of 4 (10^{-4} M, CH₃CN) with Cu²⁺
**Fig. 41.** Color changes of receptor 9 upon addition of 1 eq. of the cations. From left to right: none, Hg$^{2+}$, Cu$^{2+}$.

**Fig. 42.** UV titration of 9 ($10^{-4}$ M, CH$_3$CN) with Hg$^{2+}$

**Fig. 43.** Titration profile of 9 ($10^{-4}$ M, CH$_3$CN) with Hg$^{2+}$

**Fig. 44.** Sequential fitting of the titration profile of 9 ($10^{-4}$ M, CH$_3$CN) with Hg$^{2+}$
Fig. 45. UV titration of 9 (10^{-4} M, CH_{3}CN) with Cu^{2+}

Fig. 46. Titration profile of 9 (10^{-4} M, CH_{3}CN) with Cu^{2+}

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2009
**Fig. 47.** Color changes of receptor 8 upon addition of 1 eq. of different cations. From left to right: none, Fe$^{3+}$, Pb$^{2+}$.

**Fig. 48.** UV titration of 8 (10$^{-4}$ M, CH$_3$CN) with Fe$^{3+}$

**Fig. 49.** Titration profile of 8 (10$^{-4}$ M, CH$_3$CN/) with Fe$^{3+}$
**Fig. 50.** UV titration of $8\ (10^{-4}\ M,\ CH_3CN)$ with Pb$^{2+}$

**Fig. 51.** Titration profile of $8\ (10^{-4}\ M,\ CH_3CN)$ with Pb$^{2+}$
Fig. 52. UV titration of 2 (10^{-4} M, CH_{3}CN) with CN^{-}

Fig. 53. Titration profile of 2 (10^{-4} M, CH_{3}CN) with CN^{-}
Fig. 54. Colour changes induced by the addition of 10 eq of different anions to a solution of receptor 4 (10^{-4} M in acetonitrile). From left to right: none, F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), BzO\(^-\), NO_3\(^-\), H_2PO_4\(^-\), HSO_4\(^-\), AcO\(^-\), CN\(^-\), SCN\(^-\).

Fig. 55. UV titration of 4 (10^{-4} M, CH_3CN) with CN\(^-\)

Fig. 56. Titration profile of 4 (10^{-4} M, CH_3CN) with CN\(^-\)
**Fig. 57.** Job plot analysis of 4 (10^{-4} M in MeCN) with Cu^{2+}

**Fig. 58.** Job's plot analysis of 9 (10^{-4} M in MeCN) with Cu^{2+}
Fig. 59. Job's plot analysis of 9 (10^{-4} M in MeCN) with Hg^{2+}
5. Reversibility studies:

**Fig. 60.** (a) A solution of 4 (10^{-4} M in MeCN). (b) Addition of 4 eq of Cu^{2+} (ClO_4^-)_2 to solution (a). (c) Addition of 2 equiv of 3,6-dioxa-1,8-octanedithiole to solution (b).

**Fig. 61.** (a) A solution of 2 (10^{-4} M in MeCN). (b) Addition of 4 eq of CN^- Bu_4N^+ to solution (a). (c) Addition of 4 equiv of Ag^+ ClO_4^- to solution (b).
MS titration experiments.

Fig. 62. (a) EIMS spectrum of \( \text{2} \). (b) EIMS spectrum of \( \text{2} + 2 \) equiv \( \text{CN}^- \)
6. $^1$H NMR titration studies

**Fig. 63.** Changes induced in the $^1$H NMR spectra of 2 (200 MHz, 23 mM, CD$_3$CN, 20°C) upon addition of 1 eq of TBACN.
Fig. 64. A detailed comparison between $^1$H NMR spectra of 2 before and after addition of 1 equiv CN$^-$ (CDCl$_3$, 300 MHz)
**Fig. 65.** A detailed comparison between $^{13}$C NMR spectra of 2 before and after addition of 1 equiv CN$^-$ (CDCl$_3$, 75 MHz)
**Fig. 66.** DEPT experiment spectrum of 2 after addition of 1 equiv CN⁻ (CDCl₃, 75 MHz)
7. Kinetic studies: First order kinetics of reaction of 2 and CN⁻

Fig. 67. Plot of evolution of absorbance and time of a mixture of 2 and CN⁻ (1:1), 10⁻⁴M in CH₃CN

Fig. 68. Plot of a first order kinetics of ln(A-Aₐ) and t(s) of a mixture of 2 and CN⁻ (1:1), 10⁻⁴M in CH₃CN that afforded the constant: $K_v=0.012\text{s}^{-1}$