Electronic Supporting Information

Rational designing of first furoquinolinol based molecular systems for easy detection of Cu$^{2+}$ with potential applications in the area of membrane sensing

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Title Page..............................................................................................S1
Content Page........................................................................................S2
Analytical data..........................................................................................S3
Spectra, Figures, Tables.............................................................................S4-S30
Analytical data

**3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-c]quinolin-4-ol (FQ1).**

Yellow solid (81%), mp (decomp.) = 258-259°C, IR (KBr, cm⁻¹): ʋ_max = 3369, 2963, 2864, 2821, 1655, 1602, 1498. ¹H NMR (400 MHz, CDCl₃): δ_H = 2.47 (br s, 4H), 2.61 (br s, 2H), 3.48 (br s, 2H), 3.66 (br s, 4H), 5.26 (br s, 1H), 7.21–7.29 (m, 3H)*, 7.38 (td, 1H, J = 7.3 & 1.2 Hz), 7.54 (s, 4H), 7.82 (d, 1H, J = 7.8 Hz), 10.49 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ_c = 37.2, 48.5, 52.8, 62.2, 89.9, 103.3, 106.0, 115.1, 117.7, 120.0, 123.6, 125.9, 126.6, 128.5, 130.4, 141.0, 155.0, 155.4, 160.8. HRMS (ESI) m/z calcd. for C₂₃H₂₂BrN₃O₃ [M-H]^+ : 466.0760, found: 466.0765.

**3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-c]quinolin-4-ol (FQ2).**

Yellow solid (78%), mp = 218-220 °C, IR (KBr, cm⁻¹): ʋ_max = 2827, 1661, 1606, 1500, 1416. ¹H NMR (400 MHz, CDCl₃): δ_H = 0.87–0.94 (m, 3H), 1.36 (m, 4H), 1.64 (quint, 2H, J = 7.2 Hz), 3.39 (t, 2H, J = 7.1 Hz), 4.38 (br s, 1H), 7.14–7.26 (m, 2H)*, 7.32 (m, 2H), 7.39 (d, 2H, J = 8.5), 7.58 (dt, 2H, J = 8.5 & 1.8 Hz), 7.82 (d, 1H, J = 7.8 Hz), 11.17 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ_c = 14.0, 22.9, 29.2, 29.8, 42.6, 49.6, 107.9, 110.7, 122.4, 124.6, 128.2, 129.9, 130.4, 130.9, 131.3, 133.0, 145.7, 159.6, 160.1, 165.4. HRMS (ESI) m/z calcd. for C₂₂H₂₁ClN₂O₂[M+H]^+ : 379.1207, found: 379.1207.

* Solvent peak at 7.26 is overlapped with this peaks, hence higher integration is obtained.

See ¹H NMR spectra of both compounds at page S4 and S7 of ESI.
Figure SS1: 3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-c]quinolin-4-ol (FQ1): $^1$H NMR
Figure SS2: 3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-c]quinolin-4-ol (FQ1): $\text{^{13}C NMR}$
Figure SS3: 3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-c]quinolin-4-ol (FQ1): HRMS
Figure SS4: 3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-c]quinolin-4-ol (FQ2): $^1$H NMR
Figure SS5: 3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-c]quinolin-4-ol (FQ2): $^{13}$C NMR
Figure SS6: 3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-c]quinolin-4-ol (FQ2): HRMS
Figure S7: UV-Vis Spectra of FQ1 (20μM in DMSO:MeOH = 1:9) in the presence of different ions (10 equiv.). The distinct behaviour of Cu^{2+} (equimolar) is apparent from figure.
Figure SS8: UV-vis Spectra of FQ2 (20μM in DMSO:MeOH = 1:9) in the presence of different ions (10 equiv.). The distinct behaviour of Cu$^{2+}$ (equimolar) is apparent from figure.
Figure SS9: Fluorescence response of FQ1 (20μM in DMSO:MeOH = 1: 9) toward 10 equiv. of different metal ions after excitation at 370 nm.
Figure SS10: Fluorescence response of FQ1 (20μM in DMSO:MeOH = 1: 9) toward 10 equiv. different metal ions after excitation at 370 nm wavelength.

Fluorescence Intensity (cps)

Wavelength (nm)

FQ2, Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, K$^+$, Na$^+$, Li$^+$, Hg$^{2+}$, Fe$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Cr$^{3+}$, Gd$^{3+}$, Fe$^{3+}$, Nd$^{3+}$.
Figure SS11: Fluorescence responses of FQ1 (20μM in DMSO:MeOH = 1:9) in the presence of different metal ions.
Figure SS12: Fluorescent titration of FQ1 (20 μM in DMSO:MeOH = 1:9) against Cu^{2+} (0.1 equiv. to 2.5 equiv.) after excitation at 370 nm wavelength.

\[ Y = -865.1x + 18850 \]
\[ R^2 = 0.984 \]

LOD = 1.52 \times 10^{-7} M

\[ Y = 1.169 \times 10^{-9}x + 2.478 \times 10^{-5} \]
\[ R^2 = 0.992 \]

K = 2.11 \times 10^{4} M^{-1}
Figure SS13: Fluorescent titration of FQ2 (20 μM in DMSO:MeOH = 1:9) against Cu$^{2+}$ (0.1 equiv. to 2.5 equiv.) after excitation at 370 nm wavelength.
Figure SS14: Examination of selectivity of FQ1 (20 \( \mu \text{M} \) in DMSO:MeOH = 1:9) towards Cu\(^{2+} \) in the presence of interfering ions.
Figure S15: Examination of selectivity of FQ2 (20 μM in DMSO:MeOH = 1:9) towards Cu$^{2+}$ in the presence of interfering ions.
Figure SS16: Change in fluorescence response with time at 465 and 460 nm respectively for compounds FQ1 and FQ2.

![Graph showing fluorescence intensity over time for FQ1 and FQ2 with Cu$^{2+}$]
Figure SS17: Job’s plot to determine binding stoichiometry of compounds FQ1 with Cu$^{2+}$
Figure SS18: Job’s plot to determine binding stoichiometry of compounds FQ2 with Cu$^{2+}$
Figure SS19: HRMS of possible complex of compound FQ1 with Cu$^{2+}$

$C_{29}H_{27}Br_2CuN_3O_4S$

Calculated $M_r = 685.9385$
Figure SS20: HRMS of possible complex of compound FQ2 with Cu$^{2+}$

C$_{24}$H$_{29}$BrClCuNaN$_2$O$_3$S
Calculated $M_\text{exp} = 621.9620$
Figure SS21: Reversibility Studies
Figure SS22: NMR Titration (FQ1) in the presence of different conc. of Cu$^{2+}$ (DMSO-d$_6$ was used as NMR solvent and TMS as internal standard).

FQ1 + 1.0 equiv. Cu$^{2+}$

FQ1 + 0.5 equiv. Cu$^{2+}$

FQ1 + 0.25 equiv. Cu$^{2+}$

FQ1
Figure SS23: NMR Titration (FQ2) in the presence of different conc. of Cu$^{2+}$ (DMSO-d$_6$ was used as NMR solvent and TMS as internal standard).

- FQ2 + 1.0 equiv. Cu$^{2+}$
- FQ2 + 0.5 equiv. Cu$^{2+}$
- FQ2 + 0.25 equiv. Cu$^{2+}$
- FQ2
Figure SS24: Effect of pH on Fluorescence quenching

Fluorescence Intensity (cps)

pH
Figure SS25: DFT study (Optimized structure of FQ1 and FQ2)
Table SS1: Comparison of reported FQs with some of the recently developed sensors for Cu$^{2+}$

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sensor/probe</th>
<th>Interaction</th>
<th>Association constant ($K_a$) M$^{-1}$</th>
<th>LOD in M</th>
<th>pH range</th>
</tr>
</thead>
</table>
| 1     | FQs (This work) | Turn off (flur) Reversible | $2.11 \times 10^4$
$1.87 \times 10^4$ | $1.52 \times 10^{-7}$
$2.13 \times 10^{-7}$ | 5.5-11   |
| 2$^{st}$ | NH$_2$ NH$_2$ | Turn off (flur) Irreversible | NM | $0.5 \times 10^{-7}$ | 5-7   |
| 3$^{rd}$ | Conc. dependent Turn off (flur) | 6.82 $\times 10^4$
4.0 $\times 10^{-7}$ | NM |  |  |
| 4$^{th}$ | P-Qs | Turn on (flur) irreversible | NM | $1.5 \times 10^{-6}$ | 7-9   |
| 6$^{th}$ | Turn on (flur) | 1.1 $\times 10^{10}$
0.15 $\times 10^{-6}$ | NM |  |  |
| 7$^{th}$ | Turn off (flur) | NM | 1.27 $\times 10^{-4}$ | NM |  |
| 8$^{th}$ | Turn off (flur) | 5.0 $\times 10^4$
1.5 $\times 10^{-6}$ | 4-11 |  |  |

(flur = fluorescence, NM = Not Mentioned)
### Table SS2: Photophysical properties of FQ1 and FQ2

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Emission</th>
<th>Quantum Yield</th>
<th>Detection Limit (M)</th>
<th>Binding Constant (M⁻¹)</th>
<th>R²</th>
<th>I/I₀</th>
<th>Response Time (Min.)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>λ&lt;sub&gt;ex&lt;/sub&gt;/nm</td>
<td></td>
<td>λ&lt;sub&gt;em&lt;/sub&gt;/nm</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>FQ1</td>
<td>370</td>
<td>465</td>
<td>0.3915</td>
<td>1.52 x 10⁻⁷</td>
<td>2.11 x 10⁴</td>
<td>0.984</td>
<td>0.027</td>
</tr>
<tr>
<td>FQ1 + Cu²⁺</td>
<td>370</td>
<td>459</td>
<td>0.0253</td>
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<tr>
<td>FQ2</td>
<td>370</td>
<td>460</td>
<td>0.3856</td>
<td>2.13 x 10⁻⁷</td>
<td>1.87 x 10⁴</td>
<td>0.985</td>
<td>0.159</td>
</tr>
<tr>
<td>FQ + Cu²⁺</td>
<td>370</td>
<td>452</td>
<td>0.0597</td>
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