Supporting Information

EVALUATION OF 4,4'-DIAMINODIPHENYLMETHANE AS A PLATFORM FOR PROTON, pH, AND METAL ION RESPONSIVE FLUORESCENT PROBE.

Takaaki Miyazaki*, Shunsaku Watanabe, Shoko Oka, Taiyou Tsutumi, and Osamu Hayashida*

Department of Chemistry, Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan; email: t.miyazaki@fukuoka-u.ac.jp

Table of Contents

1. General Information .........................................................---S2
2. Proton responsiveness .....................................................---S2
3. Metal sensing ................................................................---S4
4. NMR spectra .................................................................---S7
1. General Information
Chemicals and reagents were commercially available and used without further purification, except for 2-formyl pyridine, which was purified by alumina and silica gel. $^1$H, and $^{13}$C NMR spectra were measured on a Bruker Advance III 400 spectrometer. Chemical shifts were reported in part per million (ppm) relative to TMS (0.00 ppm for $^1$H and $^{13}$C). The coupling constants ($J$) were given in hertz (Hz). MALDI-TOF mass was performed on Bruker autoflex speed. Elemental analysis was carried out with JSL JM11. Absorption spectra were recorded on a PerkinElmer Lambda 35. Fluorescence spectra were measured on a JASCO FP-750.

Relative quantum yields of 1 were estimated from eq. 1 using anthracene as a standard (in EtOH, 27%, $\lambda_{ex} = 340$ nm).

$$\phi_i = \frac{F_i f_i n_i^2}{F_s f_s n_s^2} \phi_s$$

where $\phi_i$ and $\phi_s$ are the quantum yields of the sample and the standard, respectively. $F_i$ and $F_s$ are the area of the fluorescence spectra of the sample and the standard, respectively.

2. Proton responsiveness

Figure S1. Absorption spectra of 1 (50 $\mu$M) in (a) CH$_3$CN, (b) CH$_2$Cl$_2$, and (c) toluene.

Figure S2. The reversible change of the fluorescent behavior of 1 (50 $\mu$M) by using TFA and DBU in CH$_3$CN and CH$_3$OH (1:1 v/v) ($\lambda_{ex} = 400$ nm).
Table S1. Relative quantum yield of 1 using anthracene in EtOH as a reference (27%, $\lambda_{ex} = 340$ nm).

<table>
<thead>
<tr>
<th></th>
<th>$\Phi / %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>CH$_3$CN + TFA</td>
<td>0.03</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$ + TFA</td>
<td>0.05</td>
</tr>
<tr>
<td>Toluene</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Toluene + TFA</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure S3. The partial $^1$H NMR spectra of 1 in CDCl$_3$ before (top) and after (bottom) the addition of TFA.
4. Metal sensing

Figure S4. MALDI-TOF MS of (a) 1py and (b) 1pyZn. Dithranol was used as a matrix.

Figure S5. The partial $^1$H NMR spectra of the mixture of 1 and 1py (top) and the mixture of 1 and 1pyZn (bottom) in CDCl$_3$. 
Figure S6. The partial $^1$H-$^1$H cosy spectrum of 1py in CDCl$_3$.

Figure S7. MALDI-TOF MS of (a) 1pyZn and (b) 1pyNi after fluorescence measurement. Dithranol was used as a matrix.
Figure S8. Fluorescence spectra of pyCHO and Zn(OAc)$_2$•2H$_2$O (blue), Cu(OAc)$_2$•H$_2$O (red), and Ni(OAc)$_2$•4H$_2$O (black) in MeCN and MeOH (1:1 v/v) after mixing for 1 hour.
4. NMR spectra

Figure S9. $^1$H NMR spectra of 2 in CDCl$_3$.

Figure S10. $^{13}$C NMR spectra of 2 in CDCl$_3$. 
**Figure S11.** $^1$H NMR spectra of 3 in CDCl$_3$.

**Figure S12.** $^{13}$C NMR spectra of 3 in CDCl$_3$. 

---

S8
Figure S13. $^1$H NMR spectra of 4 in CDCl$_3$.

Figure S14. $^{13}$C NMR spectra of 4 in CDCl$_3$. 
Figure S15. $^1$H NMR spectra of 1 in CDCl$_3$.

Figure S16. $^{13}$C NMR spectra of 1 in CDCl$_3$. 