Electronic Supplementary Information (ESI†)

A coumarin–dihydropyrimidine dye as a fluorescent chemosensor for hypochlorite in 99% water

Yasuhiro Shiraishi,* Chiharu Yamada and Takayuki Hirai

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

shiraish@cheng.es.osaka-u.ac.jp

CONTENTS

| Table/S | Page |
|---------|------|
| Table S1 | TD-DFT calculation results for 1, 1’ and 1” | 2 |
| Fig. S1 | $^1$H NMR chart of 1 | 4 |
| Fig. S2 | $^{13}$C NMR chart of 1 | 5 |
| Fig. S3 | FAB-MS chart of 1 | 6 |
| Fig. S4 | Absorption spectra of 1 | 7 |
| Fig. S5 | $^1$H NMR chart of 1’ | 8 |
| Fig. S6 | $^{13}$C NMR chart of 1’ | 9 |
| Fig. S7 | FAB-MS chart of 1’ | 10 |
| Fig. S8 | $^1$H–$^1$H COSY chart of 1 | 11 |
| Fig. S9 | $^1$H–$^1$H COSY chart of 1’ | 12 |
| Fig. S10 | Effect of water content on the fluorescence intensity of 1 | 13 |

Cartesian coordinates for respective compounds | 14 |
Table S1. Calculated excitation energy ($E$), wavelength ($\lambda$), and oscillator strength ($f$) for low-laying singlet state ($S_n$) of 1, 1' and 1''.[ii]

| compound | Main orbital transition (CIC [b]) | $E$ (eV) [$\lambda$ (nm)] | $f$ |
|----------|----------------------------------|----------------------------|-----|
| $S_0 \rightarrow S_1$ | HOMO $\rightarrow$ LUMO (0.70571) | 2.2918 eV [540.99 nm] | 0.0023 |
| $S_0 \rightarrow S_2$ | HOMO-1 $\rightarrow$ LUMO (0.70440) | 3.0942 eV [400.70 nm] | 0.0000 |
| $S_0 \rightarrow S_3$ | HOMO $\rightarrow$ LUMO+1 (0.70406) | 3.3076 eV [374.84 nm] | 0.0008 |
| $S_0 \rightarrow S_4$ | HOMO $\rightarrow$ LUMO+2 (0.65062) | 3.7590 eV [329.83 nm] | 0.1681 |
| $S_0 \rightarrow S_5$ | HOMO $\rightarrow$ LUMO+3 (0.66998) | 3.8658 eV [320.72 nm] | 0.0014 |
| $S_0 \rightarrow S_6$ | HOMO-2 $\rightarrow$ LUMO (0.67869) | 3.9242 eV [315.95 nm] | 0.0031 |
| $S_0 \rightarrow S_1$ | HOMO $\rightarrow$ LUMO (0.67202) | 2.5622 eV [483.90 nm] | 0.0271 |
| $S_0 \rightarrow S_2$ | HOMO $\rightarrow$ LUMO (-0.18684) | 2.8956 eV [428.17 nm] | 0.0152 |
| $S_0 \rightarrow S_3$ | HOMO-2 $\rightarrow$ LUMO+3 (-0.10524) | 3.7678 eV [329.06 nm] | 0.2785 |
| $S_0 \rightarrow S_4$ | HOMO-1 $\rightarrow$ LUMO+1 (0.12636) | 3.8169 eV [324.83 nm] | 0.172 |
| $S_0 \rightarrow S_5$ | HOMO-1 $\rightarrow$ LUMO+1 (0.20599) | 3.9169 eV [316.53 nm] | 0.0572 |
| $S_0 \rightarrow S_6$ | HOMO-3 $\rightarrow$ LUMO (0.14907) | 3.9693 eV [312.36 nm] | 0.2865 |
| $S_0 \rightarrow S_1$ | HOMO $\rightarrow$ LUMO (0.66986) | 2.8187 eV [439.87 nm] | 0.0095 |

[ii] Compound 1, 1’, and 1’’ results from computational analysis. CIC stands for compound independent coordinates.

| Transition                      | HOMO → LUMO Energy (eV) | LUMO+1 Energy (eV) | Oscillator Strength |
|--------------------------------|-------------------------|-------------------|--------------------|
| $S_0 \rightarrow S_2$          | HOMO → LUMO (-0.14003)  | 3.2523            | 0.0010             |
|                                | HOMO → LUMO+1 (0.68548) |                   |                    |
| $S_0 \rightarrow S_3$          | HOMO-1 → LUMO (0.59565) | 3.2670            | 0.2737             |
|                                | HOMO-1 → LUMO+1 (0.29465)|                   |                    |
| $S_0 \rightarrow S_4$          | HOMO-1 → LUMO (-0.27485)| 3.6413            | 0.3661             |
|                                | HOMO-1 → LUMO+1 (0.58007)|                   |                    |
|                                | HOMO-7 → LUMO (0.10009) |                   |                    |
| $S_0 \rightarrow S_5$          | HOMO-3 → LUMO+3 (0.11442)| 3.8806            | 0.1753             |
|                                | HOMO → LUMO+2 (0.63331) |                   |                    |
|                                | HOMO-3 → LUMO+1 (-0.29114)|                   |                    |
| $S_0 \rightarrow S_6$          | HOMO-1 → LUMO+2 (-0.11142)| 4.0682            | 0.1186             |
|                                | HOMO → LUMO+3 (0.61780) |                   |                    |

[a] The optimized structures for the respective models are summarized in the end of this ESI.
[b] CI expansion coefficients for the main transitions.
Fig. S1  $^1$H NMR chart of 1 (24 mM, DMSO–d$_6$, 400 MHz).
Fig. S2  $^{13}$C NMR chart of 1 (48 mM, DMSO–d$_6$, 100 MHz).
Fig. S3  FAB–MS chart of 1. (top) full and (bottom) partial charts.

$C_{21}H_{16}O_3N_2^+ (M^+) \ m/z \ 344.1158$

(Calculated: $C_{21}H_{16}O_3N_2^+ (M^+) \ m/z \ 344.1161$)
**Fig. S4**  (a) Change in absorption spectra of 1 measured at 25 °C in 1% MeCN solutions (HEPES 0.1 M, pH 7.0) with different concentration of 1. (b) Change in the absorbance at 325 nm as a function of the concentration of 1.
Fig. S5  
$^1$H NMR chart of 1’ (24 mM, DMSO–d$_6$, 400 MHz).
Fig. S6  $^{13}$C NMR chart of $1'$ (49 mM, DMSO–d$_6$, 100 MHz).
Fig. S7  FAB–MS chart of 1'. (top) full and (bottom) partial charts.

C_{21}H_{14}O_3N_2^+ (M^+) m/z 342.1003
(Calculated: C_{21}H_{14}O_3N_2^+ (M^+) m/z 342.1004)
Fig. S8  $^1$H–$^1$H COSY chart of 1 (30 mM, DMSO–d$_6$, 400 MHz). Colored circles indicate the observed cross peaks. The texts next to the circle mean the coupling protons.
Fig. S9  $^1$H-$^1$H COSY chart of 1' (30 mM, DMSO–d$_6$, 400 MHz). Colored circles indicate the observed cross peaks. The texts next to the circle mean the coupling protons.
Fig. S10  Time-dependent change in the fluorescence intensity of 1 at 462 nm (10 μM) after addition of OCl(⁻) (50 equiv) measured at 25 °C in MeCN solutions (HEPES 0.1 M, pH 7.0) with different water contents.
Cartesian Coordinates (in Å) of 1 (DFT/B3LYP/6–31+G*)

| Atom | X  | Y  | Z     | Atom | X  | Y  | Z     |
|------|----|----|-------|------|----|----|-------|
| C    | -2.59998 | 2.665419 | -0.00016 | C    | 3.059685 | -0.05288 | -2.43551 |
| C    | -1.30104 | 2.122463 | -0.00013 | H    | -2.72707 | 3.746045 | -0.00022 |
| C    | -1.10217 | 0.727232 | -3.1E-05 | H    | -4.69881 | 2.275944 | -0.00012 |
| C    | -2.25129 | -0.08475 | 0.000018 | H    | -5.22576 | -2.56471 | 0.000175 |
| C    | -3.5653  | 0.436016 | -1.2E-05 | H    | 0.169034 | -0.99211 | 0.000113 |
| C    | -3.70712 | 1.835229 | 0.00001  | H    | -0.49296 | 3.859368 | -0.00026 |
| O    | -2.04423 | -1.43422 | 0.000097 | H    | -6.29185 | 0.645239 | 0.883376 |
| C    | -3.08388 | -2.37208 | 0.00018  | H    | -6.29183 | 0.645076 | -0.88353 |
| C    | -4.4286  | -1.82921 | 0.00013  | H    | -6.81258 | -0.8015  | 0.000053 |
| C    | -4.68196 | -0.4931  | 0.00039  | H    | 0.53197  | 0.374526 | 2.045974 |
| C    | 0.283028 | 0.10234  | 0.000012 | H    | 0.531927 | 0.374141 | -2.046   |
| O    | -0.21267 | 2.930196 | -0.00019 | H    | 2.539396 | 0.096748 | 3.379357 |
| C    | -6.09647 | 0.0244   | -1.8E-05 | H    | 4.939409 | -0.5332  | 3.380705 |
| O    | -2.7745  | -3.54241 | 0.000175 | H    | 6.165051 | -0.8784  | 1.257772 |
| N    | 1.043652 | 0.518103 | 1.182202 | H    | 6.165027 | -0.87863 | -1.25769 |
| C    | 2.379962 | 0.110716 | 1.236732 | H    | 4.939344 | -0.53382 | -3.38066 |
| C    | 3.066915 | -0.08666 | 0       | H    | 2.539331 | 0.096131 | -3.37938 |
| C    | 2.379938 | 0.110493 | -1.23675 | N    | 1.043627 | 0.517892 | -1.18227 |
| C    | 3.059732 | -0.05244 | 2.435509 | C    | 4.426643 | -0.40805 | 2.429927 |
| C    | 5.113351 | -0.60361 | 1.248362 | C    | 4.452032 | -0.44108 | 0.00002  |
| C    | 5.113327 | -0.60384 | -1.24831 | C    | 4.426596 | -0.4085  | -2.42989 |
Cartesian Coordinates (in Å) of 1' (DFT/B3LYP/6-31+G*)

|   | C   | C   |   | C   | C   |   | C   | C   |   |   | C   | C   |   |   | H   | H   |
|---|-----|-----|---|-----|-----|---|-----|-----|---|---|-----|-----|---|---|-----|-----|
|   | -2.39828 | 2.535728 | 0.004035 | O   | 0.468111 | -3.3021 | 0.001439 |
|   | -3.77172 | 2.877929 | 0.004016 | H   | -1.63685 | 3.314675 | 0.005575 |
|   | -4.76072 | 1.911836 | 0.002177 | H   | -4.04639 | 3.932516 | 0.005508 |
|   | -4.41637 | 0.529281 | 0.002422 | H   | -5.81255 | 2.196413 | 0.002197 |
|   | -3.03233 | 0.179967 | 0.0024  | H   | -6.43152 | -0.28443 | -0.00179 |
|   | -2.04167 | 1.196913 | 0.002172 | H   | -5.69292 | -2.64723 | -0.00507 |
|   | -5.36951 | -0.52877 | -0.00175 | H   | -3.26806 | -3.23395 | -0.00498 |
|   | -4.95165 | -1.84821 | -0.00358 | H   | 4.800607 | -2.23354 | 0.002606 |
|   | -3.57993 | -2.1905 | -0.00354 | H   | 2.934406 | -3.84995 | 0.002979 |
|   | -2.62046 | -1.18539 | -0.00166 | H   | 4.992548 | 2.628992 | -0.00221 |
| N | -1.25928 | -1.49611 | -0.00159 | H   | 6.247798 | -0.50404 | 0.88488 |
|   | -0.35063 | -0.54241 | 0.000165 | H   | 6.248926 | -0.5056 | -0.88068 |
| N | -0.7061 | 0.774861 | 0.002072 | H   | 6.670849 | 0.977479 | 0.00106 |
|   | 1.076946 | -0.95218 | 0.000509 | H   | -0.4405 | -2.81595 | -9.1E-05 |
| C | 2.178517 | -0.05788 | -0.00022 | H   | 0.02803 | 1.473898 | 0.003469 |
|   | 3.521757 | -0.47823 | 0.000672 |   |   |   |   |
| C | 3.776708 | -1.86895 | 0.001968 |   |   |   |   |
|   | 2.744403 | -2.77822 | 0.002216 |   |   |   |   |
| C | 1.40121 | -2.34592 | 0.001351 |   |   |   |   |
| O | 1.90004 | 1.282537 | -0.00205 |   |   |   |   |
| C | 2.871409 | 2.285091 | -0.00329 |   |   |   |   |
| C | 4.236283 | 1.846849 | -0.00165 |   |   |   |   |
| C | 4.569175 | 0.521925 | 0.000124 |   |   |   |   |
| C | 6.01435 | 0.103494 | 0.001417 |   |   |   |   |
| O | 2.454138 | 3.435226 | -0.00571 |   |   |   |   |
Cartesian Coordinates (in Å) of 1" (DFT/B3LYP/6–31+G*)

|   | C   | C   | C   | C   | C   | C   | C   | O   | O   | O   |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|   | 2.37416 | 2.522559 | -0.00129 | 0.483158 | -3.3102 | -0.00283 |
|   | -3.7451 | 2.878156 | -0.00031 | -1.60664 | 3.295546 | -0.0021 |
|   | -4.74181 | 1.92105 | 0.000792 | -4.00934 | 3.935198 | -0.00041 |
|   | -4.4108 | 0.53598 | 0.000971 | -5.7911 | 2.214756 | 0.001571 |
|   | -3.03094 | 0.177156 | -3.5E-05 | -6.43313 | -0.259 | 0.002969 |
|   | -2.03019 | 1.183408 | -0.00114 | -5.71618 | -2.62907 | 0.003345 |
|   | -5.37365 | -0.51358 | 0.002171 | -3.29944 | -3.23985 | 0.001656 |
|   | -4.96965 | -1.83544 | 0.002371 | 4.815675 | -2.22837 | 0.002315 |
|   | -3.59918 | -2.1923 | 0.001382 | 2.979776 | -3.86025 | 0.000617 |
|   | -2.64666 | -1.18944 | 0.00161 | 4.980906 | 2.638133 | 0.002026 |
|   | -1.27325 | -1.46935 | -0.00077 | 6.249434 | -0.48788 | 0.885605 |
|   | -0.30687 | -0.53777 | -0.00158 | 6.251229 | -0.48776 | -0.87957 |
|   | -0.68937 | 0.758337 | -0.00192 | 6.661218 | 0.997367 | 0.003554 |
|   | 1.084074 | -0.97029 | -0.0016 | 0.044764 | 1.459333 | -0.00241 |
|   | 2.183708 | -0.0667 | -0.00094 | -0.89967 | -2.44376 | -0.00078 |
|   | 3.526125 | -0.47506 | 0.000374 | 0.890955 | -0.48776 | -0.87957 |
|   | 3.786633 | -1.87659 | 0.001054 | 6.249434 | -0.48788 | 0.885605 |
|   | 2.77247 | -2.79149 | 0.000165 | 6.251229 | -0.48776 | -0.87957 |
|   | 1.386249 | -2.4033 | -0.00182 | 6.661218 | 0.997367 | 0.003554 |
|   | 1.897803 | 1.271479 | -0.00137 | 6.661218 | 0.997367 | 0.003554 |
|   | 2.864031 | 2.286576 | -0.00023 | 4.225091 | 1.855903 | 0.001149 |
|   | 4.225091 | 1.855903 | 0.001149 | 4.56151 | 0.526302 | 0.001369 |
|   | 6.01094 | 0.118632 | 0.00282 | 6.01094 | 0.118632 | 0.00282 |
|   | 2.429016 | 3.432491 | -0.00014 | 2.429016 | 3.432491 | -0.00014 |