Supporting Information

for

AIE-Active Bis-Cyanostilbene-Based Organogels for Quantitative Fluorescence Sensing of CO₂ based on Molecular Recognition Principles

Yao Ma,^a Massimo Cametti,^{*b} Zoran Džolić ^c and Shimei Jiang^{*a}

 ^a State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, 2699 Qianjin Avenue, Changchun 130012, P. R. China; Fax: +86-431-85193421; Tel: +86-431-85168474; E-mail: smjiang@jlu.edu.cn
^b Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milano, Italy; E-mail: massimo.cametti@polimi.it
^c Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia.

	Contents	Page
1	Materials and methods, synthesis of 1	S3–S4
2	¹ H and ¹³ C-NMR spectra of 1	S5
3	AIE properties of 1	S6
4	Gelation properties of 1	S7
5	Temperature-dependent FT-IR spectra of the xerogel	S8
6	¹ H-NMR spectral changes of 1 upon titration with different anions in DMSO- d_6 solution	S9
7	¹ H-NMR spectra of the toluene- d_8 gel of 1 in the presence of varying amounts of CIL and (TBA)Cl	S10
8	¹ H and ¹³ C-NMR spectra of CIL	S11
9	Effect of DEA to 1 monitored by ¹ H-NMR	S12
10	Gel-aggregates made by different amines: photos and their fluorescent spectra	S13

11	DLS data of gel aggregates with different fractions of DEA (v/v).	S14
12	Calculaions of the detection limit	S15
13	$^1\text{H-NMR}$ spectra of the gel aggregates upon adding different volumes of CO_2 in toluene-d_8	S16
14	SEM and TEM images of the xerogel film	S17
15	Details of the various steps of the xerogel film preparation and CO_{2} response setup	S18
16	Emission spectra of xerogel films and corresponding photographs on successive addition of (TBA)Cl to the gel and after drying (illumination under 365 nm)	S19
17	Fluorescent images of the gel aggregate samples exposed to different volumes of CO_2 and the films from the corresponding samples after drying and their emission spectra (illumination under 365 nm)	S20
18	The selectivity to CO_2 compared with other gases and the response to CO_2 in the presence of other gases	S21
19	Time dependence of fluorescent intensity of the xerogel film at 460 nm put to work sensing CO_2 in a laboratory facility	S22
20	Time dependence of fluorescent intensity of the xerogel film at 460 nm detecting CO_2 gas in a crowded classroom	S23
21	Comparison between the detector reading and our system's performance in determining the $\rm CO_2$ concentration	S24
22	Additional references	S25

Materials and Methods

All reagents and solvents are obtained from commercial supplies and used directly without further purification unless otherwise stated. The solvents for spectroscopic studies are purified according to standard methods. The ¹H and ¹³C-NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts, in ppm, are referred to TMS as internal standard. UV-Vis absorption spectra were recorded on a Shimadzu 3600 UV-Vis-near-IR spectrophotometer. The solvents for spectroscopic studies were spectroscopic grade and used as received. Fluorescence spectroscopic studies were performed on a Shimadzu RF-5301PC spectrofluorometer. SEM images were obtained from a JEOL JEM-6700F scanning electron microscope with 3 kV operating voltage. TEM was performed on a JEOL JEM-2100F transmission electron microscope. Samples were prepared by wiping a small amount of gel samples onto a carbon-coated copper grid followed by naturally evaporating the solvent. The thickness of xerogel films was measured using a Veevo Dektak 150 profiler. FT-IR was conducted on a Bruker Optics VERTEX 80 v Fourier transform infrared spectrometer. Elemental analysis was was carried out using a Vario micro cube elemental analyser. MALDI-MS was carried on a Brucker Autoflex speed TOF/TOF mass analyzer.

N,N'-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-hexadecyloxyisophthalamide (1)

5-(hexadecyloxy)isophthalic acid¹ (0.2 g, 0.49 mmol) and dry N,N'-DMF (10 µL, 0.13 mmol) were dissolved in dry CH₂Cl₂ (20 mL) under N₂ atmosphere and to it oxalyl chloride (0.10 mL, 1.08 mmol) was added dropwise. The reaction mixture was stirred for 30 minutes at room temperature and then was refluxed for 1 hr. After cooling the reaction mixture, solvent was removed under reduced pressure to yield a light green solid which was dried thoroughly under vacuum and used in the next step without further purification.

2-Phenyl-3-(4-aminophenyl)acrylonitrile² (0.32 g, 1.46 mmol) and triethylamine (0.20 mL, 1.46 mmol) were dissolved in dry CH_2Cl_2 (30 mL). A solution of 5-(hexadecyloxy)isophthaloyl dichloride in dry CH_2Cl_2 (15 mL) was added dropwise for 1 hr while the mixture was stirred vigorously under a nitrogen atmosphere. The reaction mixture was refluxed for 5 hrs. The solvent was evaporated in vacuo to yield a red oil. The residue was taken up in ethanol (50 mL)

S3

to precipitate the product. The precipitate was filtered and washed for several times with ethanol and water, respectively. The product was obtained as a yellow solid (0.34 g, yield 86%). M.p.: 192 °C; FT-IR (KBr) v/cm⁻¹ =3324, 3258, 2921, 2850, 1656, 1587, 1513, 1318; ¹H-NMR (500 MHz, DMSO- d_6) δ /ppm = 10.70 (s, 2H, -CONH), 8.17 (s, 1H, ArH), 8.01 (d, *J* = 9.8, 10H, ArH), 7.78 (d, *J* = 7.7, 4H, ArH), 7.74 (s, 2H, -CH=), 7.53 (t, *J* = 7.6, 4H, ArH), 7.45 (t, *J* = 7.2, 2H, ArH), 4.16 (t, *J* = 6.1, 2H, -CH₂), 1.84 - 1.75 (m, 2H, -CH₂), 1.47 (s, 2H, -CH₂), 1.23 (s, 24H, -CH₂), 0.84 (t, *J* = 6.7, 3H, -CH₃); ¹³C-NMR (126 MHz, DMSO- d_6) δ /ppm = 14.36, 22.56, 25.98, 29.10, 29.22, 29.53, 31.78, 68.67, 108.91, 117.32. 118.67, 119.95, 120.66, 126.08, 129.47, 129.61, 130.48, 134.53, 136.68, 141.69, 142.74, 159.14, 165.42; Anal. Calcd for C₅₄H₅₈N₄O₃: C, 79.97; H, 7.21; N, 6.91. Found: C, 80.09; H, 7.18; N, 6.85. MALDI-MS: Calcd for **1**: 810.451; Found [**1** + Na]⁺: 833.424.



Figure S1. ¹H-NMR spectrum of hexadecyloxyisophthalamide (1) in DMSO- d_6 .

N,N'-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-



Figure S2. ¹³C-NMR spectrum of N,N'-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-hexadecyloxyisophthalamide (**1**) in DMSO- d_6 .



Figure S3. a) UV-Vis and b) fluorescent spectra of **1** (10^{-5} M) in THF / H₂O mixtures with different solvent ratios. The red shifting on UV-Vis spectra indicates the molecule stacking in J-aggregates. The increasing intensity on fluorescent spectra indicates **1** has AIE property.

Gelation experiment

In a typical gelation test, a weighed amount of the gelator was mixed with a measured volume of the selected solvent in a test tube, which was capped and heated in an oil bath until the compound dissolved. After the solution was allowed to stand at room temperature, the sample was sonicated for ca. 60 seconds. Finally the test tubes were inverted to observe whether the content of the tube could still flow or not, thus the formation of gel (G), insoluble material (I), or solution (S) was determined.

Table S1. Gelation properties and critical gelator concentrations (cgcs') of **1** in various organic solvents at 25 °C.^[a]

Solvent		Solvent	
Methanol	I	DMF	S
Ethyl acetate	I	1,4-Dioxane	S
Cyclohexane	I	Benzene	G (3.6)
<i>n</i> -Hexane	I	Toluene	G (3.3)
Acetone	I	<i>o</i> -Xylene	G (3.3)
Acetonitrile	I	<i>m</i> -Xylene	G (3.5)
Dichloromethane	I	<i>p</i> -Xylene	G (3.7)
THF	S	Chlorobenzene	G (7.7)
DMSO	S	Bromobenzene	G (8.3)

^[a] The values in parentheses are cgc (mg mL⁻¹). G: gel; S: solution; I: insoluble.



Figure S4. Temperature-dependent FT-IR spectra of the xerogel of 1 from toluene.



Figure S5. Stacked partial ¹H-NMR spectra (DMSO- d_6 : D₂O 98:2) for the titration of **1** [5x10⁻³ M] with a) CIL, b) (TBA)Cl, c) (TBA)Br and d) (TBA)I at 300 K. Arrows indicate increasing anion concentrations.



Figure S6. Partial ¹H-NMR of the toluene- d_8 gel (containing 5 µL DMSO- d_6) of **1** in the presence of varying amounts of a) CIL and b) (TBA)Cl.



Figure S7. a) ¹H-NMR spectral changes of DEA upon titration of CO_2 with CIL formation; b) ¹³C-NMR spectrum of CIL in $CDCl_3$.



Figure S8. ¹H-NMR spectra of **1** in DMSO- d_6 (5 x 10⁻³ M) upon addition of increasing amounts of DEA (from bottom to top) at 300 K. No apparent specific interaction with DEA can be detected.



Figure S9. a) Photographs showing the changes in the toluene gel of **1** (10 mg mL⁻¹) after the addition of diethylamine (DEA, v/v) under daylight (top) and UV-light illumination (middle); b) Fluorescent spectra of the gel aggregates with different fractions of DEA (v/v); c) Fluorescent spectra of the gel aggregates with different fractions of aniline; d) Fluorescent spectra of the gel-aggregates with 2% aniline upon bubbling increasing amounts of CO₂ (λ_{ex} = 365 nm); Inset: Plot of the intensity at 458 nm versus CO₂ equivalents; e) Fluorescent spectra of the gel-aggregates with different fractions of n-butylamine; f) Fluorescent spectra of the gel-aggregates with 2% n-butylamine upon bubbling increasing amounts of CO₂ (λ_{ex} = 365 nm); Inset: Plot of the intensity at 459 nm versus CO₂ equivalents.



Figure S10. DLS data of gel aggregates obtained by adding different fractions of DEA in the toluene gel of 1 (v/v).



Figure S11. Plot of the intensity of the gel-aggregates at 455 nm versus different concentrations of CO₂ ($I : I_{455 \text{ nm}}$, C: concentration of CO₂). The detection limit was calculated based on reported works.³ It was calculated following the equation: Detection limit = $3\sigma/k$; σ is the standard deviation (It is calculated based on the fluorescent intensities of the gel-aggegates recorded for ten times), and k is the slope between the intensity $I_{455 \text{ nm}}$ versus the concentration of CO₂. The detection limit was calculated to be about 3.715 x 10⁻⁵ M (ca. 908 ppm).



Figure S12. ¹H-NMR spectra of the gel aggregates upon adding different volumes of CO_2 in toluene- d_8 .



Figure S13. SEM and TEM images of the xerogel film of **1** made by drop-casting method (slow-evaporation from its hot toluene solution, 10^{-3} M).



Figure S14. Photographs of a) the preparation of the xerogel film by drop-casting; b) CO_2 response setup (the xerogel film was sealed in a quartz vial in the presence of DEA vapor) and c) the method of CO_2 concentration controlling.

Preparation of the xerogel films and corresponding CO₂ response setup.

Xerogel films were fabricated on quartz templates (0.8 cm × 3cm) from a hot solution of **1** in toluene (10^{-3} M) by drop-casting method. The thickness of the films was measured as ca. 1.2 µm. Commercial quartz vessels (size: 4 mL) were firstly blown with sufficient N₂ gas to drive inside air away. The xerogel films were sealed in the 4 mL quartz vessels with plastic caps. 0.3 mL DEA was added into the bottom of the vessels by 1 mL glass injectors. Later, different amounts of CO₂ gas was added also though glass injectors. Thus the standard plot of sensing CO₂ gas and the detection limit were gained.

For real applications, the atmosphere of 4 mL quartz vessel was firstly fully exchanged with the target gas or environment (over 300 mL) instead of N₂. And a xerogel film was sealed in the vessel quickly with a plastic cap. 0.3 mL DEA was then injected by a glass injector. The fluorescent intensity of the xerogel film at 460 nm was monitored with time. Through measuring the values of the film at the beginning and the end, the CO₂ concentration of the target gas or environment was calculated utilizing the formula given by the standard plot.



Figure S15. Emission spectra of xerogel films and corresponding photographs of **1** upon successive addition of (TBA)Cl to the gel and after drying (under illumination at 365 nm).



Figure S16. a) Fluorescent images of the gel aggregate samples exposed to different volumes of CO_2 and the films from the corresponding samples after drying; b) and their corresponding fluorescent spectra.



Figure S17. a) The selectivity to CO_2 compared with other gases (the film is exposed to sufficient target gas in the presence of DEA vapor) and b) the response to CO_2 in the presence of other gases (The first bar refers to exposing to pure interference gas. The second and the third bar refer to exposing to the mixture gases. The mixture gases are composed by 20% or 1% fraction of interference gas with 80% or 99% CO_2 gas. Blank is one filled with N₂ gas).



Figure S18. Time dependence of fluorescent intensity of the xerogel film at 460 nm put to work at sensing CO_2 in a real case scenario, *i.e.*, a laboratory facility. I / I_0 value can be used to determine CO_2 concentration.



Figure S19. Time dependence of fluorescent intensity of the xerogel films at 460 nm when detecting CO_2 gas in a crowded classroom at different time intervals: a) 8:30; b) 9:30; c) 10:30; d) 11:30; e) 14:00.



Figure S20. Comparison between the detector reading and our system's performance in determining the CO_2 concentration in three samples at known CO_2 concentration (500, 1000 and 1600 ppm). We employed the HORIBA automotive emission analyzer MEXA-584L.

References:

- S1) W. L. Lim, C. W. Oo and T. Kobayashi, J. Appl. Polym. Sci., 2015, 132, 41504.
- S2) Y.-S. Zheng and Y.-J. Hu, J. Org. Chem., 2009, 74, 5660.
- S3) (a) Z. Guo, N. R. Song, J. H. Moon, M. Kim, E. J. Jun, J. Choi, J. Y. Lee, C. W. Bielawski, J. L. Sessler and J. Yoon, *J. Am. Chem. Soc.*, 2012, **134**, 17846; (b) G. Xia, Y. Liu, B. Ye, J. Sun and H. Wang, *Chem. Commun.*, 2015, **51**, 13802.