Supplementary Information

Synergy of CO_2-response and Aggregation Induced Emission in a Small Molecule: Renewable Liquid and Solid CO_2 Chemosensors with High Sensitivity and Visibility

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1. Video S1: Fluorescence change and recovery cycle of TPE-amidine-L

An about 3-minute length of video file was provided: Video S1.mp4

2. Video S2: Fluorescence change and recovery cycle of CO_2 sensing “tape” (TPE-amidine-S)

An about 6-minutes length of video file was provided: Video S2.mp4

3. Video S3: CO_2 sensing “tape” (TPE-amidine-S) thickness, flexibility and adhesion

An about 1-minutes length of video file was provided: Video S3.mp4

4. Fluorescent sensors for CO_2

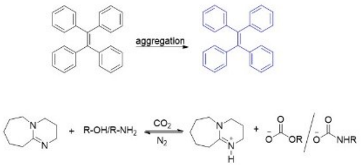
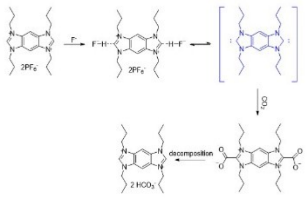
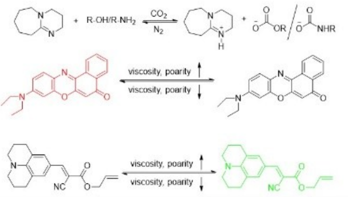
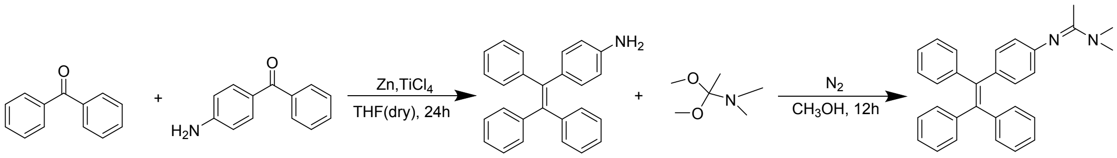
Design principle	Fluorescent unit	Detection mechanism	Example
Aggregate-induced emission (AIE)-based fluorescent sensor	AIE type molecule	CO_2 induced the systematic physico-chemical change of the molecule (aggregation or disaggregation) or the medium (polarity, viscosity, *etc*), which in turn influences the fluorescent ability.	
Anion-activated fluorescent sensor	N-heterocyclic carbenes and their derivatives	NHCs are often produced by deprotonating the corresponding imidazolium salts, has a intrinsic ability to active CO_2 to form imidazolium carboxylates.	
Intra-molecular hydrogen bond-based fluorescent sensor	Amino acid and their derivatives	Amino acids and their derivatives can react with CO_2 to form carbamic acids. The intra-molecular hydrogen bond-based fluorescent sensor is based on the photoinduced electronic transfer (PET) effect and the special ability of amino acid.	
Multidye-based small-molecule fluorescent sensor	Charge transfer dye and molecular rotor dye	CO_2 induced the systematic physico-chemical change of the the medium (polarity, viscosity, *etc*), which in turn influences the dye's fluorescent ability.	

Table S1. Brief introduction of the sorts of CO_2 fluorescent sensors based on different design principle.

5. Synthesis of TPE-amidine

TPE-amidine was synthesized according to Scheme S1.

Synthesis and characterization



Scheme S1. Synthesis route of TPE-amidine

5.1 Synthesis of 1-(4-Aminophenyl)-1,2,2-triphenylethene (TPE-NH_2)

A 250 mL flask charged with Zn powder (1.28 g, 19.6 mmol) and ultra-dry THF (50 mL) was placed in an ice-water mixture under continuous stirring with a magnetic stirring bar. After purging the flask with N_2 gas, 1.04 ml of $TiCl_4$ was added slowly with a constant pressure drop funnel under the temperature range of 0-10℃. Consequently, the reaction mixture was stirred in room temperature for 30 minutes and then refluxed for 2.5 h. After the mixture was cooled to room-temperature, 0.4 mL of pyridine was added into the flask slowly. 0.2 g of benzophenone (1.1 mmol) and 0.18 g of 4-aminobenzophenone (1.0 mmol) were dissolved in 5 mL THF and then added into the flask slowly within 30 minutes. The mixture was refluxed at 70 ℃ for 24 h and cooled to room-temperature. 10% K_2CO_3 solution was added to terminate the reaction and the solvent was removed using rotary evaporation. The residue was added to water and was extracted twice with dichloromethane (DCM). Finally, the organic phase was dried with MgSO4. The crude product was purified by silica-gel column chromatography using DCM/PE (1/3, v/v) as eluent. The target molecular 1-(4-Aminophenyl)-1,2,2-triphenylethene (TPE-NH_2) was obtained in 53% yield (0.22 g) based on benzophenone. ^1H NMR (600 MHz, Chloroform-d) δ 7.08 (d, J = 20.3 Hz, 15H), 6.86 (s, 2H), 6.47 (s, 2H), 3.65 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 144.66 , 144.26 , 132.56 , 131.54 , 131.47 , 131.43 , 127.74 , 127.62 , 127.59 , 126.32 , 126.14 , 114.45. Q-Exactive LC-MS calcd for $[M^+ H]^+$: 348.17468; found: 348.17474. ^1H NMR, ^{13}C NMR and Mass spectra of TPE-NH_2 was shown in Figure S-1, S-2, and S-3, respectively.

5.2 Synthesis of N,N-dimethyl-N'-(4-(1,2,2-triphenylvinyl)phenyl)acetimidamide (TPE-amidine)

TPE-NH_2 (0.100 g, 0.288 mmol) and 1,1-dimethoxy-N,N-dimethylethan-1-amine (0.115 g, 0.864 mmol) and methanol (0.2 ml) were stirred at 65 ℃ for 12h under N_2 atmosphere. Solvent was removed under reduced pressure, followed by chromatography using a silica gel column (CH_2Cl_2:PE, 3:1, v:v). The product was further heated at 65℃ on high vacuum for 8h to afford TPE-amidine (N,N-dimethyl-N'-(4-(1,2,2-triphenylvinyl)phenyl)acetimidamide) as a yellow solid in 92.4% yield (0.110 g) based on 1-(4-Aminophenyl)-1,2,2-triphenylethene. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.09 (d, J = 33.9 Hz, 15H), 6.91 (s, 2H), 6.48 (s, 2H), 3.03 (s, 6H), 1.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.36, 150.62, 144.27, 144.17, 141.28, 139.70, 136.86, 131.93, 131.52, 131.46, 127.61, 127.51, 126.26, 126.15, 126.10, 121.82, 38.02, 14.99. Q-Exactive LC-MS calcd for $[M^+ H]^+$: 417.23253; found: 417.23233.^{1}H NMR, ^{13}C NMR and Mass spectra of TPE-NH_2 was shown in Figure S-4, S-5 and S-6, respectively.

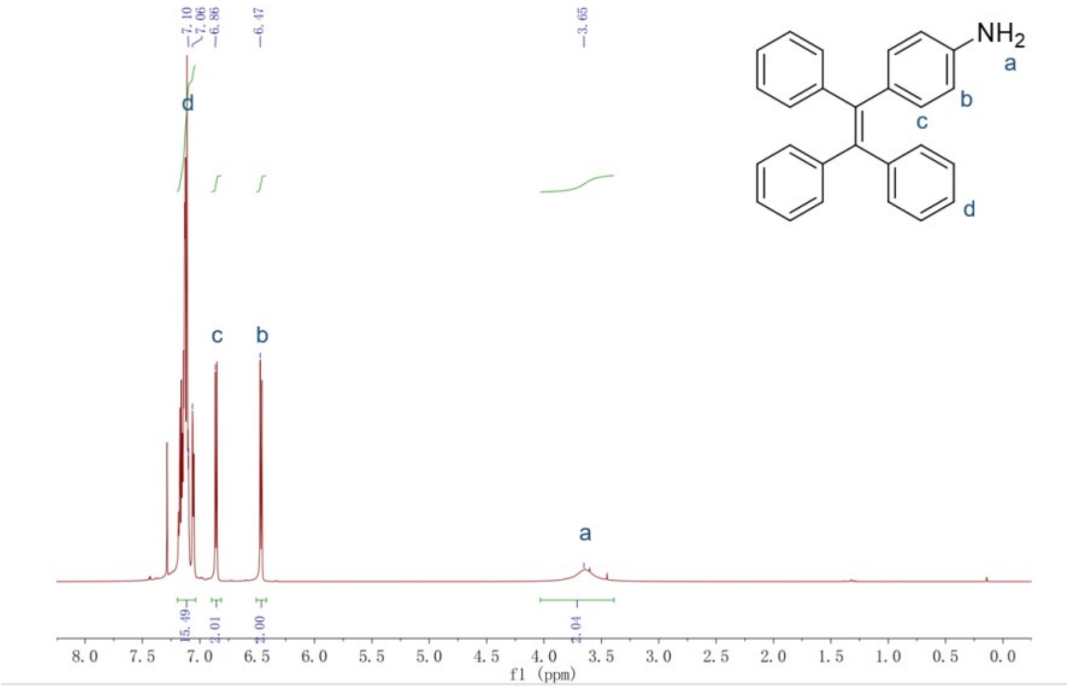


Figure S-1. ^{1}H NMR spectrum of TPE-NH_2 (chloroform-d)

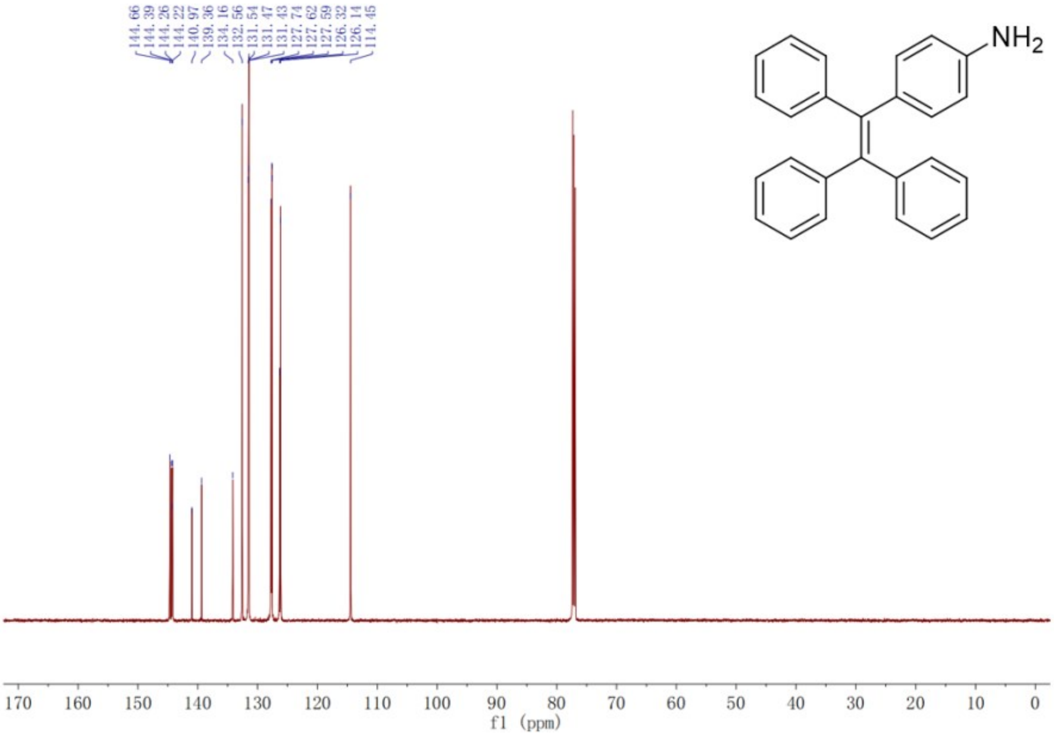


Figure S-2. ^{13}C NMR spectrum of TPE-NH_2 (chloroform-d)

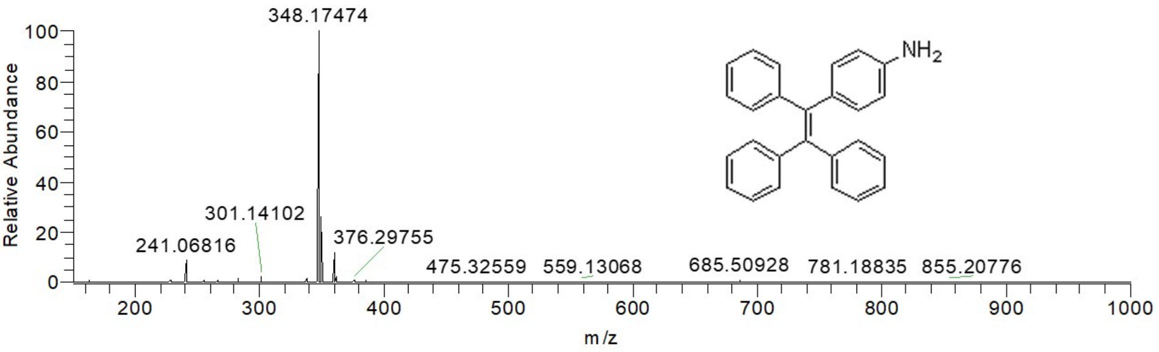


Figure S-3. Mass spectrum of TPE-NH$_2$ (calculated for $C_{26}H_{21}N$ [M$^+$H]$^+$ 346.17468, found 348.17474)

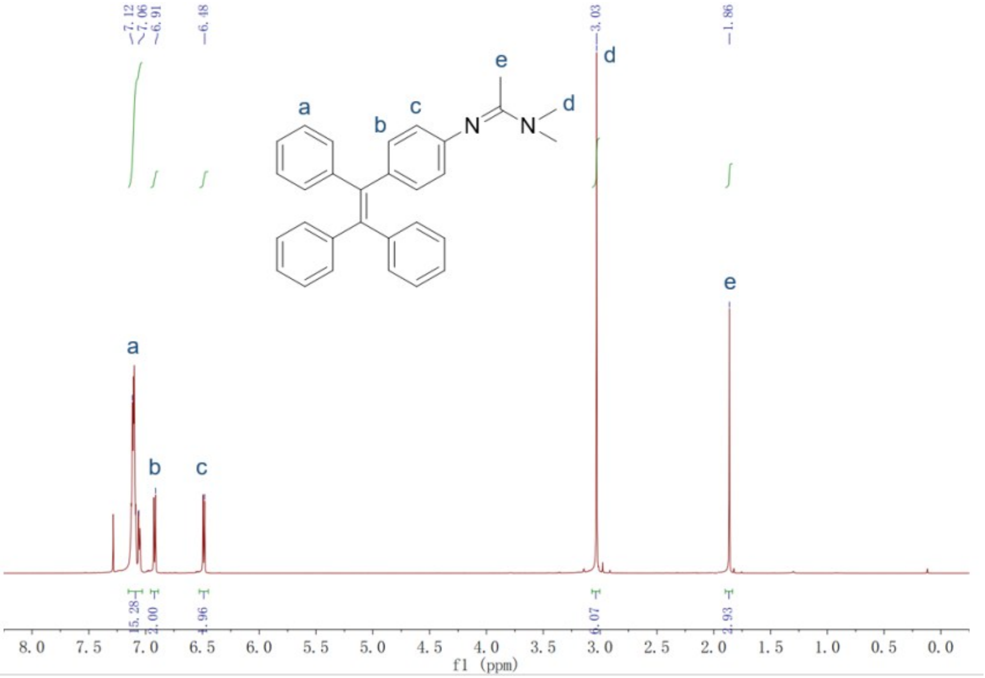


Figure S-4. ^{1}H NMR spectrum of TPE-amidine (chloroform-d)

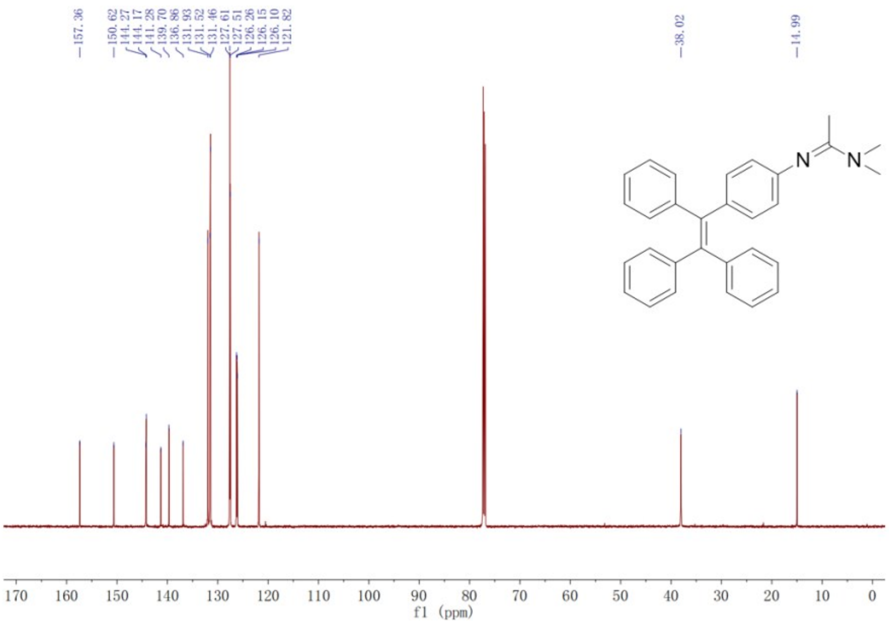


Figure S-5. ^{13}C NMR spectrum of TPE-amidine (chloroform-d)

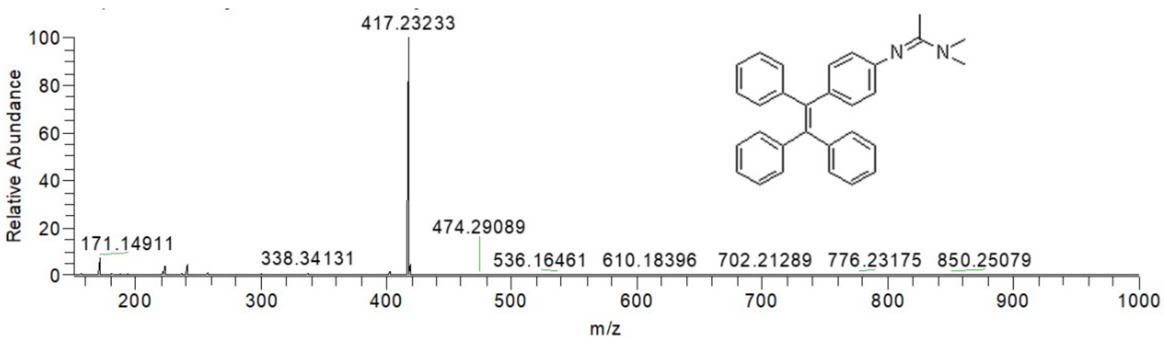


Figure S-6. Mass spectrum of TPE-NH$_2$ (calculated for $C_{30}H_{28}N_2$ $[M^{+}H]^{+}$ 417.23253, found 417.23233)

6. The size distribution of nanoparticles of TPE-amidine

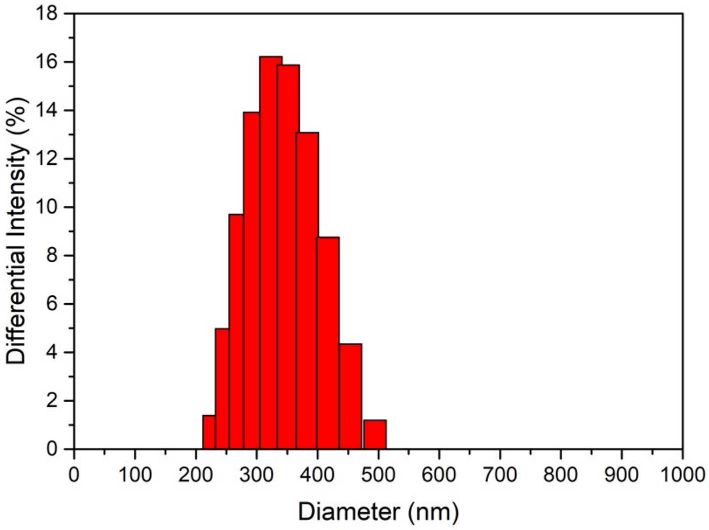


Figure S-7. The size distribution of nanoparticles of TPE-amidine (100 μM) in DMF/H_2O (1/9, v/v, 3ml) mixture.

7. Transmittance changes of TPE-amidine-L

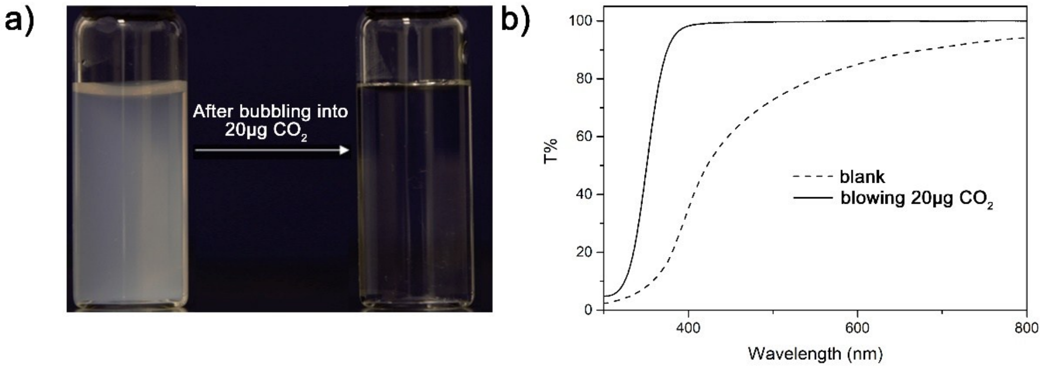


Figure S-8. (a) Photographs of TPE-amidine-L before (left) and after (after) being bubbled into 20 μg CO_2; (b) Transmittance changes of TPE-amidine-L

8. Determination of limit of detection (LOD)

$$LOD = 3 \times \left(\frac{rms_{noise}}{slope}\right) \qquad \textbf{(Formula S1)}$$

Where “slope” is the k of curve equation and rms_{noise} represents the standard deviation for maximum FL intensity (500 nm) of the fluorescent probe in the absence of carbon dioxide.

$Y_{ppm} = -0.01038 - 0.0001V_{CO2}$ (R^2=0.99426)

LOD = 3 * 0.000820 / 0.0001 (ppm) = 24.6 ppm

9. Fluorescence change of CO_2 sensing “tape” (TPE-amidine-S)

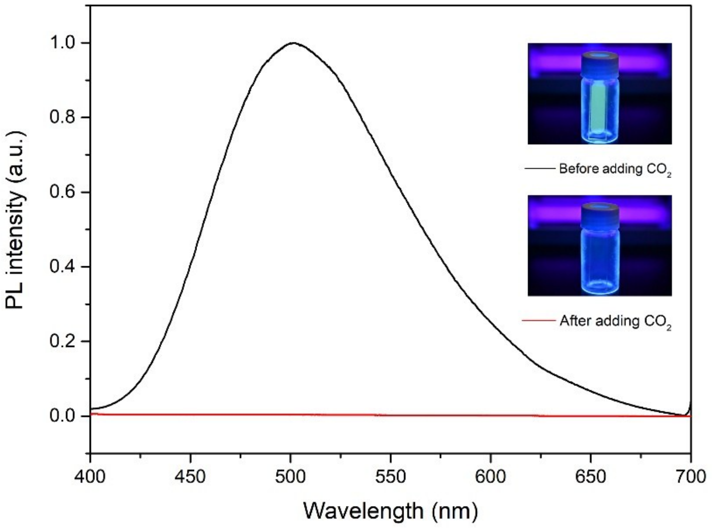


Figure S-9. Fluorescence spectra of CO_2 sensing “tape” (TPE-amidine-S) before and after exposing to CO_2 vapor.