

Electronic Supplementary Information (ESI)

Molecular combination between alkanolamines and galvinol for ratiometric colorimetric sensing of CO₂ gas

Ajay Kumar Sharma,^{a,b} Poonam Sharma,^{a,b} Pushkar Mehara^{a,b} and Pralay Das^{*a,b}

^a Chemical Technology Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur-176061, H.P., India, Fax: +91-1894-230433, *E-mail: pdas@ihbt.res.in, pralaydas1976@gmail.com

^b Academy of Scientific and Innovative Research (AcSIR), Ghaziabad- 201002, India

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General Information:

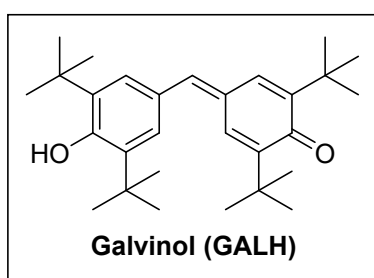
Butylated hydroxyl toluene (BHT), tetrabutylammonium fluoride (TBAF) other reagents and solvents (CH₃CN, THF, acetone, MEA, DEA, and TEA) used in this study were purchased from Sigma-Aldrich, Avra synthesis, Sd Fine-chem Ltd., and Central Drug House (CDH) Pvt. Ltd. Companies. Reactions were monitored by thin layer chromatography (TLC) which was performed using pre-coated silica gel plates 60F254 (Merck) in a UV light detector. ESI-MS spectra were recorded using a Waters micro mass Q-TOF Ultima Spectrometer. ¹H and ¹³C NMR spectra were recorded using a Jeol India (Model: JNM ECX -500) NMR spectrometer operating at 500 MHz (¹H) and 125 MHz (¹³C). The spectra were recorded at 25 °C in CDCl₃ [residual CHCl₃ (δ_{H} 7.26 ppm) and CHCl₃ (δ_{C} 77.00 ppm)]. Chemical shifts were recorded in δ (ppm) relative to the TMS and NMR solvent signal. Coupling constants (*J*) are given in Hz and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet. Deionized water was prepared by the Milli-Q water ion exchange system and was used for performing water cross-sensitivity experiments. The UV-Vis absorption spectra were recorded through NanoDrop 2000 UV-Vis spectrophotometer (Thermo Scientific™). FT-IR spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer in the 4000-400 cm⁻¹ wavelength region. ESI-MS spectra were recorded using high-resolution 6560 Ion Mobility Q-TOF LC/MS (Agilent, Santa Clara, USA). The melting point range of synthesized compounds was recorded using visual melting range instrument {LABINDIA (MR-VIS⁺)}. The CO₂ gas measurement was performed by mass flow controller (Alicat Mass Flow Controller Mode: MC-100SCCM-D-DB9M/5M, 5IN, RIN, LVD, RVD) having standard Accuracy: $\pm 0.6\%$ of reading OR $\pm 0.1\%$ of full scale, whichever is greater.

Procedure for synthesis of galvinol: The synthesis of galvinol was performed by our previously developed method, i.e. 100 mg (0.45 mmol) of butylated hydroxytoluene (BHT) was heated with 1.2 equivalents (0.54 mmol) of tetrabutylammonium fluoride (TBAF) on a magnetic stirrer using 1.0 mL acetonitrile (CH₃CN) solvent at 130 °C in a 50 mL round bottom flask (RBF) under an open-air environment in a fume hood. It may be noted that the boiling point of CH₃CN solvent is 82 °C and evaporates after some time leaving a deep purple colour paste behind. Therefore, to maintain the homogeneity of the reaction mixture during the interval of 5-hour reaction time, 2.0 mL of CH₃CN solvent was further added at the time interval of 1.5 hours. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was cooled to room temperature, and a thick purple colour paste was obtained. The reaction mixture was subjected to acidic workup with the

help of dil. HCl (4N) during which the purple colour immediately converted to an oily thick brownish layer. Water was added to the reaction mixture and the organic mixture was extracted with ethyl acetate (5 X 2 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under a vacuum. The resulting residue was directly purified by column chromatography on silica gel using pure n-hexane as eluent to give the galvinol as the final product.

Characterization data for galvinol and by-products obtained (¹H, ¹³C NMR, HRMS, and GC-MS):

2,6-di-tert-butyl-4-(3,5-di-tert-butyl-4-hydroxy benzylidene)cyclohexane-2,5-dien-1-one (or Galvinol):

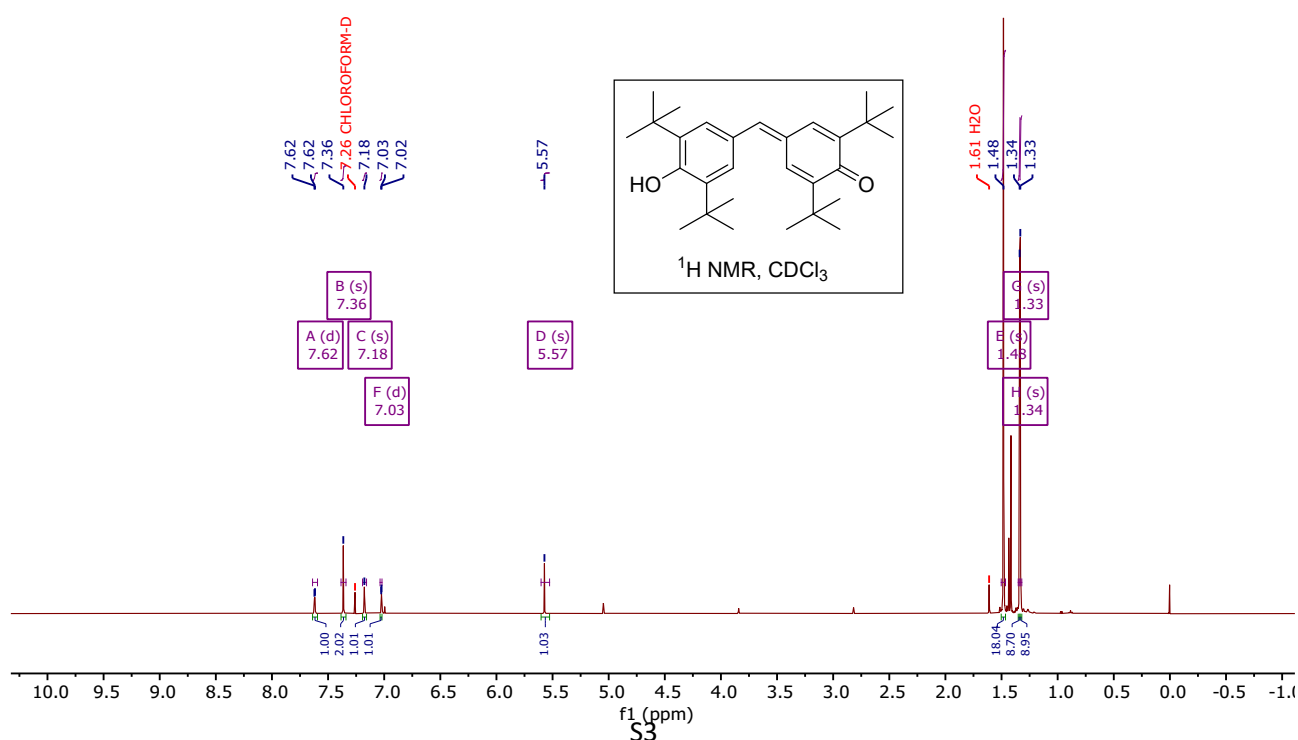


Yield: 0.45 mmol scale, 52.0 mg, 55 % isolated yield. (Yellow solid, Melting point: 154-156 °C).

¹H NMR (CDCl₃, 600 MHz): δ 7.62 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.36 [s, 2H, {CHC(CH₃)₃}₂], 7.18 (s, 1H, Ar-CH=C), 7.03 (d, *J* = 1.4 Hz, 1H, Ar-H), 5.57 (s, 1H, OH), 1.48 [s, 18H, (CH₃)₃], 1.34 [s, 9H, (CH₃)₃], and 1.33 [s, 9H, (CH₃)₃].

¹³C NMR (CDCl₃, 151 MHz): δ 186.54, 155.60, 148.82, 146.92, 144.65, 136.50, 135.79, 129.98, 128.29, 127.68, 35.57, 35.05, 34.54, 30.35, 29.77, 29.63.

HRMS (APCI/TOF): Calculated for (C₂₉H₄₂O₂+H⁺): 423.3258. Found: 423.3236.



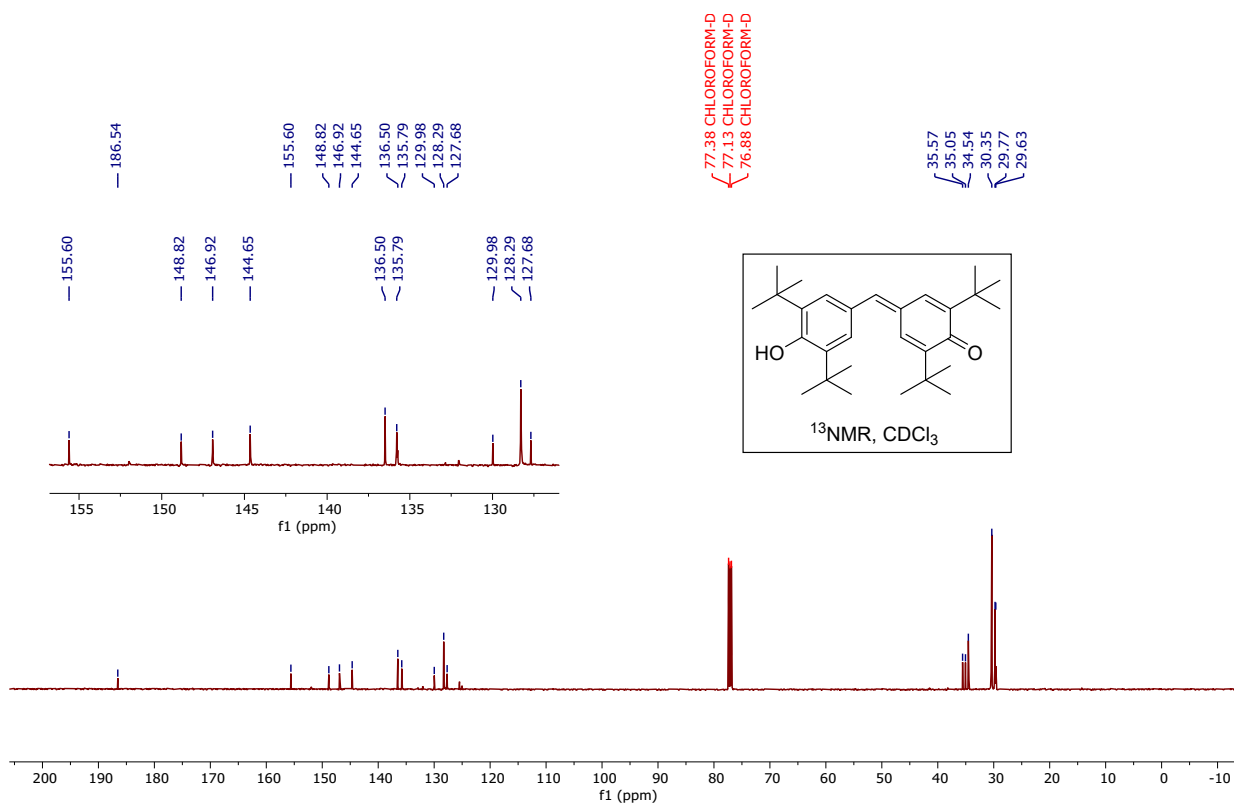


Figure S1. ¹H & ¹³C NMR spectra of galvinol.

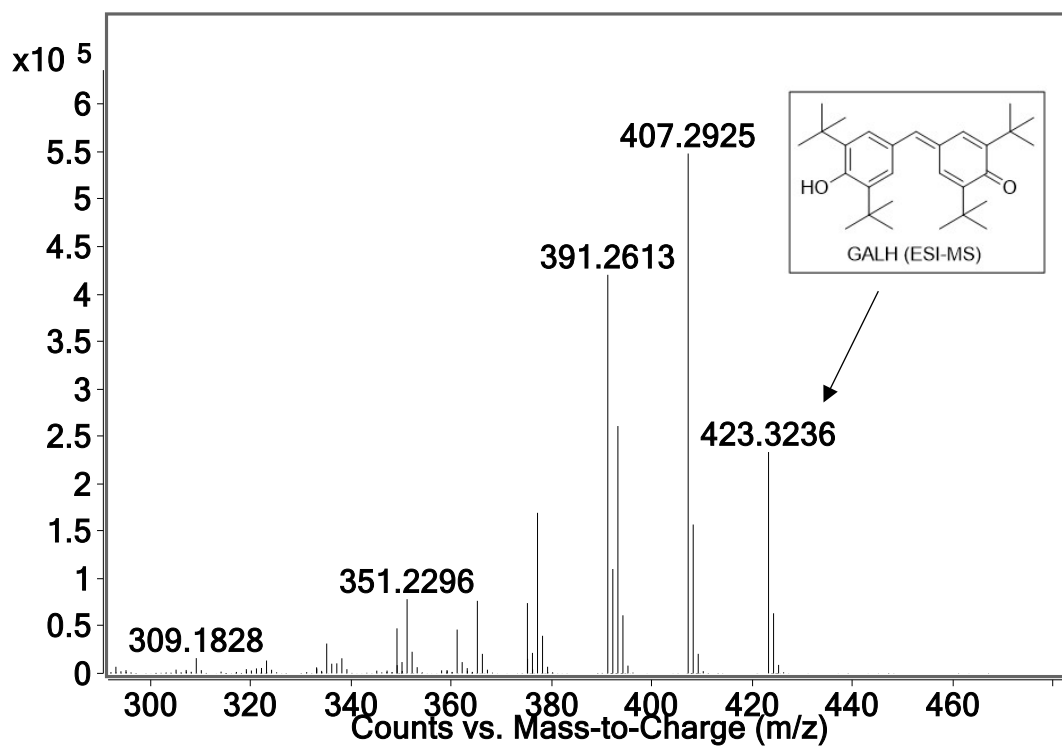
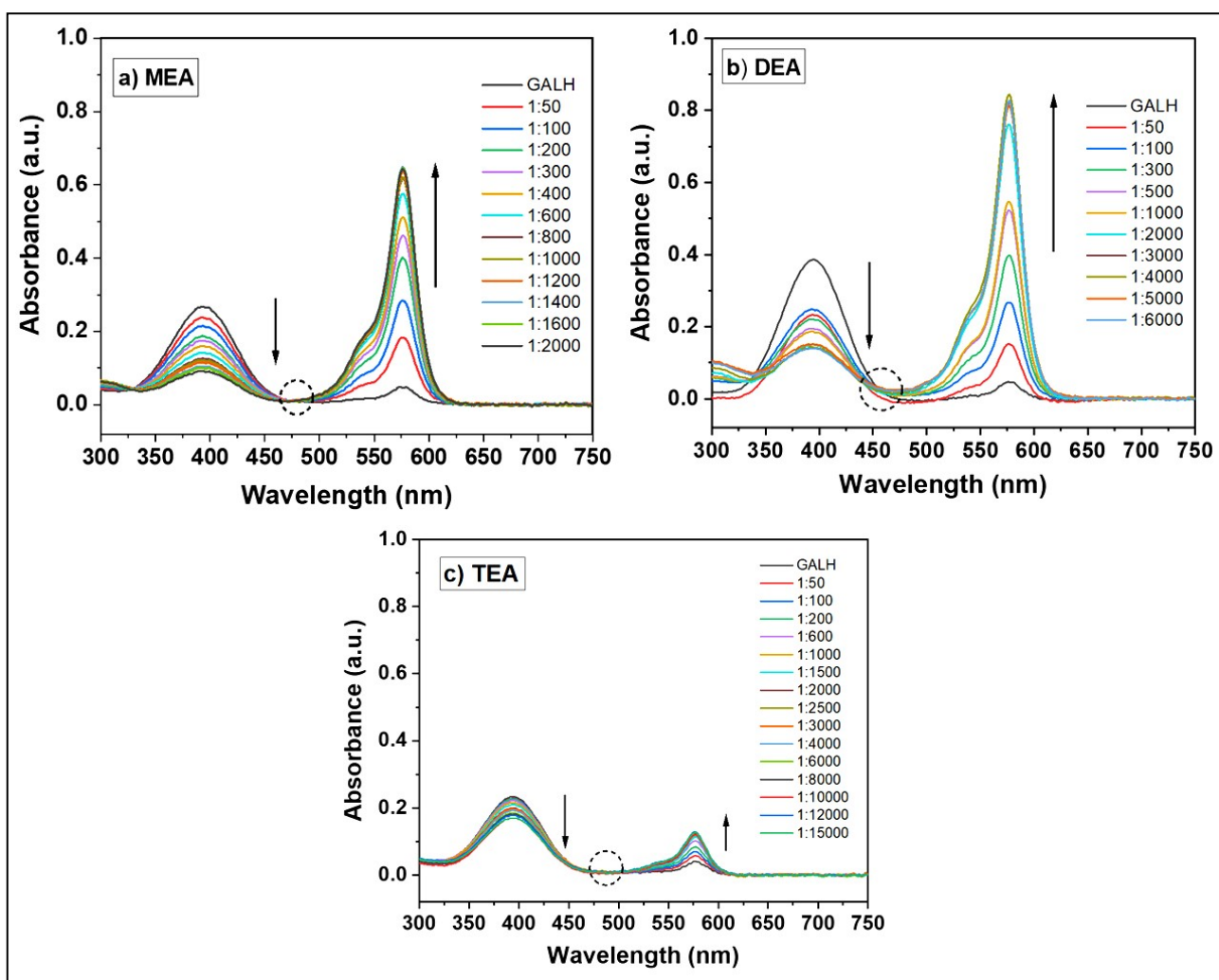


Figure S2. HRMS (ESI) spectra of galvinol.

General procedure for spectroscopic measurements

Titration of galvinol with fluoride Ion:

The alkanolamines concentration required for the ionization of galvinol (GALH) was determined by systematic UV-Vis absorbance spectroscopic titration in CH_3CN solvent. For UV-Vis spectroscopic measurements 10.0 mM GALH solution was prepared in dry CH_3CN solvent and was further diluted to 8 μM by adding 0.8 μL to 999.2 μL solution of different MEA, DEA and TEA concentrations prepared in dry CH_3CN solvent to give 1.0 mL of GAL-MEA, GAL-DEA and GAL-TEA respectively. The study revealed that 2000 equivalents of MEA and 6000 equivalents of DEA were



sufficient with respect to GALH (8 μM) for obtaining an absorption maximum at 577 nm due to GALH deprotonation (Figure S3a-b). Furthermore, TEA addition was not able to deprotonate GALH even when it was added in 15000 equivalents to that of GALH (8 μM) (Figure S3c, Table S1).

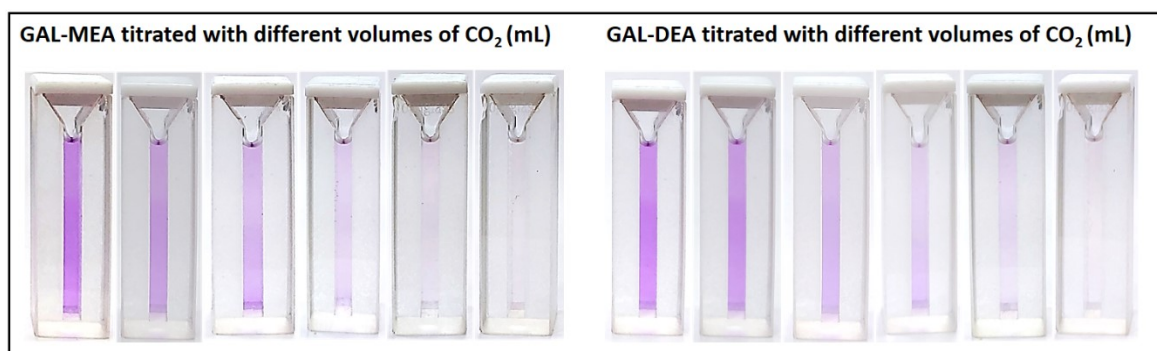
Figure S3. Optimization for complete ionization of galvinol in alkanolamines (a) MEA, (b) DEA, and (c) TEA.

Table S1: MEA, DEA and TEA concentration optimization for galvinol ionization in CH₃CN

Alkanolamine	Concentration for GALH ionization (8 μM)	Composition
MEA	16 mM	1:2000 (GAL-MEA)
DEA	48 mM	1:6000 (GAL-DEA)
TEA	Tested up to 120 mM	1:15000 (GAL-TEA), Poor ionization

solvent

Solvent	GAL-MEA			GAL-DEA		
	Ionization	CO ₂ Response	Recyclability	Ionization	CO ₂ Response	Recyclability
CH ₃ CN	Yes	Yes	Yes	Yes	Yes	Yes
THF	No	-	-	No	-	-
DMSO	Yes	Very poor	-	Yes	Very poor	-
Acetone	Yes	Yes	No	Yes	Yes	Very poor

**Table S2:** Solvents (polar aprotic) screening for CO₂ sensor development**Figure S4.** GAL-MEA and GAL-DEA treated with increasing order of CO₂ gas volume (mL).**Table S3:** UV-vis spectra wavelength changes of GAL- MEA and GAL-DEA in CH₃CN

Parameter	GAL-MEA (GALH: MEA = 1: 2000)	GAL-MEA +CO ₂	GAL-DEA (GALH: DEA = 1: 6000)	GAL-DEA +CO ₂
Wavelength	577 nm	392 nm	577 nm	392 nm
Blue shift	185 nm		185 nm	
Isosbestic point	470-485 nm		475-485 nm	

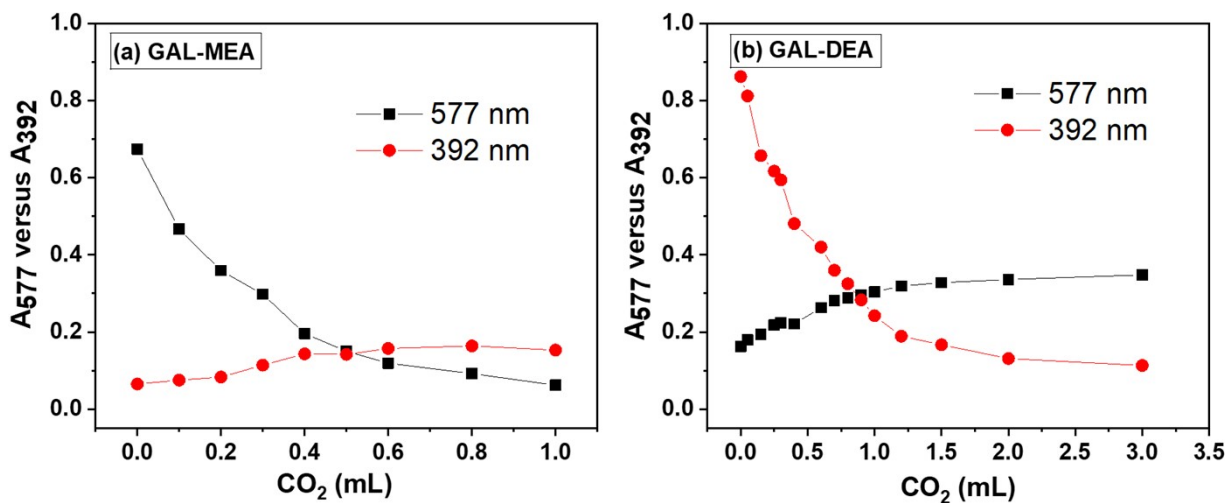


Figure S5: Ratiometric change for GAL-MEA (a) and GAL-DEA (b) on titration with CO₂.

LOD calculations:

The LOD was calculated by using the formula = $3\sigma/m$

Where σ is the standard deviation of the blank samples (i.e. GAL-MEA and GAL-DEA) and m is the slope calculated from the logarithm of the absorbance ratio calibration curve; A stands for absorbance peak intensity.

(a) GAL-MEA in CH₃CN (1.0 mL):

$$A = 2.04298 [\text{CO}_2] - 1.01475$$

$$R^2 = 0.99185, \text{CO}_2 = 0-0.5 \text{ mL}$$

$$\text{As, LOD} = 3\sigma/m$$

Where, σ = Standard deviation of blank solution (GAL-MEA) measured by 10 times;

$$m = 2.04298$$

$$\text{LOD} = 19 \text{ ppm}$$

(b) GAL-DEA in CH₃CN (1.0 mL):

$$A = 0.79056[\text{CO}_2] - 0.6731$$

$$R^2 = 0.99057, \text{CO}_2 = 0- 1.0 \text{ mL}$$

$$\text{As, LOD} = 3\sigma/m$$

Where, σ = Standard deviation of blank solution (GAL-DEA) measured by 10 times;



$m = 0.79056$

LOD = 31 ppm

Figure S6: Mass flow controller used for CO₂ volume (mL) measurement.

pH interference study for GAL-MEA and GAL-DEA probes:

The pH interference study for GAL-MEA and GAL-DEA probes in CH₃CN solvent using buffer solutions of different pH (potassium hydrogen phthalate/benzethonium chloride for pH 3.0-5.0, potassium dihydrogen phosphate/ disodium hydrogen phosphate/benzethonium chloride for pH 6.0-7.0, sodium tetraborate decahydrate/benzethonium chloride for pH 8.0-10.2 adjusted with the help of H₃PO₄/NaOH). The absorption maximum of GAL-MEA and GAL-DEA in CH₃CN at 577 nm in 1% v/v water and of 1% v/v respective buffer solution was compared.

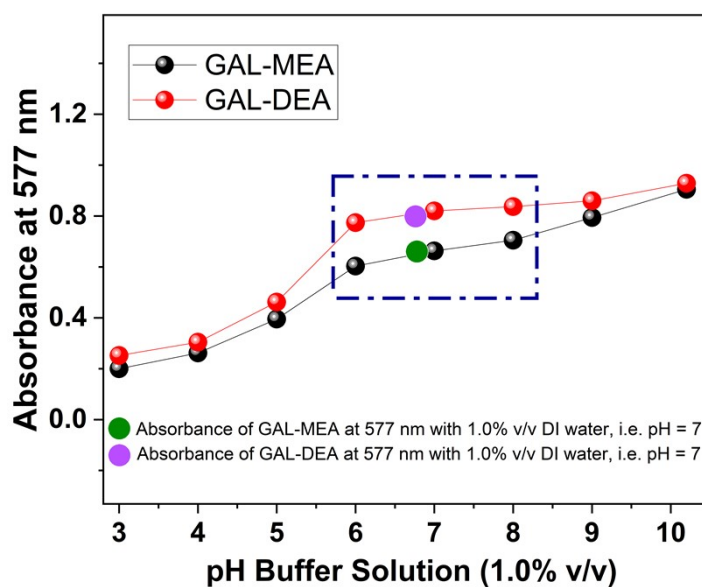


Figure S7: pH interference study for GAL-MEA and GAL-DEA probes.

Table S4: Comparison of key sensor parameters of present work with previously published colorimetric CO₂ sensor development-based reports

Sr. No.	Sensing material components	Limit of detection (LOD) and detection range (ppm or %)	Reversible	Humidity (or water) Cross sensitivity	Water as part of sensor	Major advantages	References
1	Polydiacetylene, functionalized with amines and imidazolium groups in 0.5% aqueous triethylamine	Found sensitive to detection atmospheric level of CO ₂ (i.e. 400 ppm)	No	-	Yes	Naked-eye colorimetric and fluorometric CO ₂ detection	<i>J. Am. Chem. Soc.</i> 2013, 135 , 17751-17754
2	Tetrapropyl benzobisimidazolium salt and tetrabutylammonium fluoride in CH ₃ CN solvent	~30 ppm	No	-	No	Naked-eye colorimetric and fluorometric CO ₂ detection	<i>J. Am. Chem. Soc.</i> , 2012, 134 , 17846-17849
3	Cresol red pH-indicator dye and tertiary amino alcohols immobilized on a porous γ -aluminium oxide support	>400 ppm and range 500- 2600 ppm	Yes	No	No	Solid-state sensors for CO ₂ and SO ₂ detection	<i>J. Mater. Chem. A</i> , 2015, 3 , 5642-5647
4	Thiol and amine groups functionalized silica nanoparticles with squaraine dye	~120 ppm	No	-	Yes	Naked-eye colorimetric CO ₂ detection	<i>Chem. Eur. J.</i> , 2013, 19 , 17301-17304
5	<i>m</i> -cresol purple, tetraoctyl ammonium hydroxide, ethylcellulose, tributylphosphate, glass slide.	Detection range 0-4% dissolved CO ₂	Yes	Yes	Yes	Plasticized and unplasticized polymer colorimetric film sensors for CO ₂ gas detection	<i>Sensors and Actuators B</i> . 1994, 21 , 83-89
6	<i>m</i> -cresol purple,	-	Yes	Minor	Yes	Thermoplastic	<i>J. Mater. Chem.</i>

	hydrophobic silica, tetrabutylammonium hydroxide					incorporated CO ₂ -sensitive pigments	2010, 20,5008–5010
7	pH indicator cresol red encapsulated in gas-permeable membrane and acryl reactor	Detection range 0.1-30% CO ₂ in soil	Yes	-	Yes	Colorimetric CO ₂ sensors for large scale monitoring sites	<i>Science of The Total Environment</i> 2020, 729 , 138786
8	Neutral red, phenol red and <i>m</i> -cresol purple solution	LOD as ~1.98 ppm in the range of 50–120 ppm	Yes	Yes	Yes	Colorimetric detection of CO ₂ in low concentration	<i>3 Biotech.</i> 2022, 12 , 334
9	Alkanolamines (MEA and DEA) and galvinol in CH ₃ CN solvent	LOD as ~19 ppm in GAL-MEA and range upto 1808 ppm; ~31 ppm in GAL-DEA and range upto 5409 ppm	Yes	Negligible	No	New molecular system, Low-cost, easy to fabricate, Rapid response for very low CO ₂ concentrations	Present work