Supporting information

"Turn-off" fluorescence probe for the selective determination of pendimethalin using mechanistic docking model of novel oxacalix[4]arene

Manthan Panchal[a], Mohd. Athar[b], P. C. Jha[b], Anita Kongor[a], Viren Mehta[a], Keyur Bhatt[c], Vinod Jain[a]*

[a]Department of Chemistry, School of Sciences, Gujarat University, Navrangpura, Ahmedabad-380009, India.
[b]CCG@CUG Group,School of Chemical Sciences, Central University of Gujarat, Sector-30, Gandhinagar-382030, India.
[C]Department of Chemistry, C.U. Shah University, Wadhwan-363030, Gujarat, India.

Contents

1. Materials and method

Unless otherwise stated, DC,triethylamine was purchased from Sigma-Aldrich (USA).Fluorescence-active TLC plates (F-2009) and silica gel were acquired from Merck. All pesticides and solvents employed were commercially available and were used as received without further purification. The melting points (uncorrected) were measured with a VEEGO (Model; VMP-DS) melting point apparatus (Mumbai, India).Elemental analysis (C, H and N) was performed on varioMICRO-Variant elemental analyzer (Mt.Laurel, USA).1H NMR and 13C NMR spectra was scanned on 500 MHz and 100 MHz respectively on a FT-NMR model Bruker, Avance II at 298 K with TMS as the internal reference (Ettlingen, Germany). ESI-Mass spectra analyzed taken on a micromassQuarter2 mass spectrometer (Utah, USA). The ultraviolet absorption spectra were examined in the range of 200–800 nm using a Jasco V-570 UV–Vis recording spectrophotometer (Tokyo, Japan). The fluorescence spectra and relative fluorescence intensities were measured on spectra obtained on by a Jasco FP-8300 spectrofluorometer (Xenon lamp head Xe900) (Tokyo, Japan).

2. Synthesis procedure

Synthesis of Bi-dansylated Oxacalixarene (BDO)

As shown in scheme 1, oxacalixarene [1](0.2g,0.24mmol) was made soluble in dry acetone(20ml),to which triethyl amine (TEA) was added with vigorous stirring, and the reaction mixture was stirred for1 h at room temperature. A solution of DC (0.1ml, 0.96mmol)in dry acetone was added to the reaction mixture and was stirred at room temperature for 24 h. The solvent was evaporated in vacuo. The crude was thus obtained and was subjected to column chromatography using silica gel with EtOAc: hexane (3:7) as the eluent. The fractions were separated, dried, and recrystallized in alcohol to give BDO. **Yield,** 0.28 g (78%).**Elemental analysis** for $C_{48}H_{34}N_6O_{18}S_2$: Calcd. C;55.07%, H;3.27%,N;8.03%; S;6.13%, Found: C;55.13%, H; 3.39%, N;8.17%, S; 6.02%.**UV absorption λ max (methanol)nm**: 251 nm.**^{1}H NMR (500 MHz, DMSO**) δ (ppm): 8.58 (d, 1H), 8.26 (s, 1H), 8.18 (d, 1H), 7.68 (m, 4H), 7.48 (d, 2H), 7.29 (t, 1H), 7.13 (d, 1H), 2.87 (s, 6H).**^{13}C NMR (100 MHz, DMSO)**: 154.31, 141.30, 140.85, 128.09, 115.40, 100.86, 44.91, 44.69 ppm.**MS (ESI-MS): *m/z*,** 1047 $[M+H]^{+1}$.

3. Generalprocedureforthedetectionofpesticidesbyspectrophotometryand spectrofluorimetry:

The same concentration (4×10^{-5}M) of BDO stock solution and various pesticides (Ametryn, Simetryn, Sulfosulfuron, Propanil, Pretilachlor, Tebuconazole, Terbutryn, Metalaxyl, Clodinafop Propargyl, Simazine, Thiophanate methyl, PM, Tricyclazole, and Atrazine)were prepared in MeOH. A 2.5ml aliquot of the stock solution of the BDO and a 2.5ml aliquot of the stock solution of each pesticides were added to5 ml volumetric flasks, so that the effective concentration of BDO and the pesticides was 2×10^{-5}M. The absorption spectra in the presence of other pesticide solutions and that of BDO were compared.

An emission titration study was per formed using the same stock solution of fluoroionophore (BDO) with different pesticides. To prepare the reaction mixtures, 2.5 ml of each pesticide solution was added to a 5 ml volumetric flask. Comparison of the fluorescence spectra of theprepared solutions and that of the BDO was then performed.

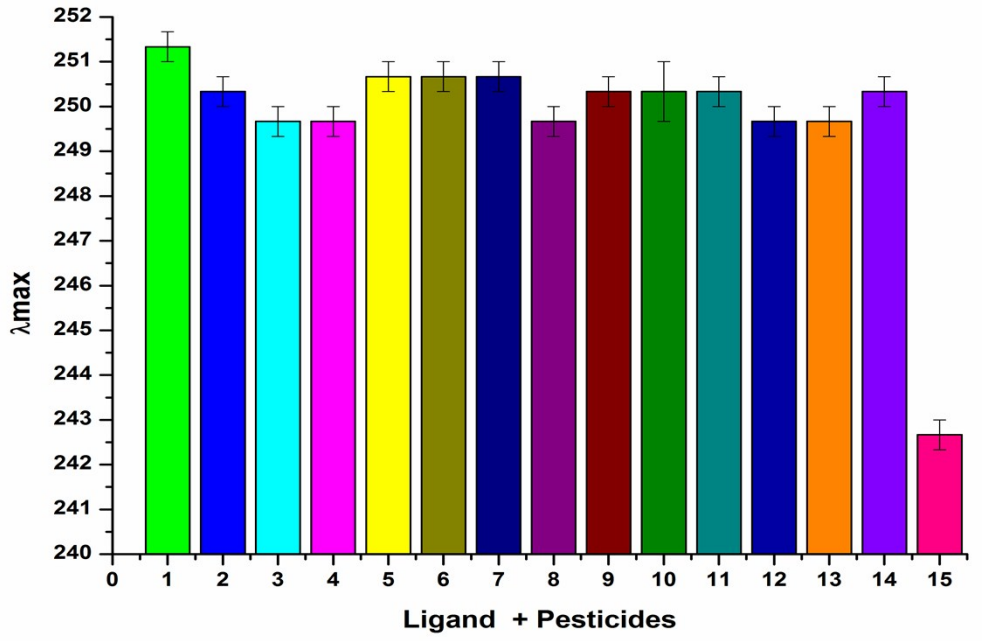

Fig. S1 Graphical representation of significant change in λmax of BDO (4×10^{-5} M) upon the addition of various pesticides in methanol (4×10^{-5} M)

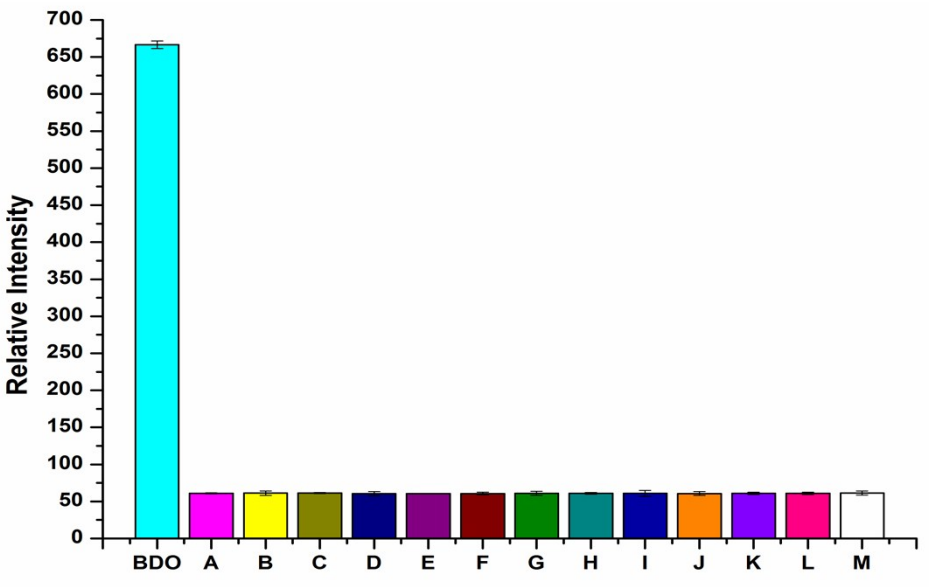

Fig. S2 Competitive emission spectra of BDO with PMin presence of other pesticides (A= BDO+PM, B = A+ Propanil, B = A+ Pretilachlor, C = A+ Sulfosulfuron, D = A+Ametryn, E = A+ Tebuconazole, F = A+ Terbutryn, G = A+ Atrazine, H = A+ Clodinafop Propargyl, I = A+ Metalaxyl, J = A+ Thiophanate methyl, K = A+ Tricyclazole, L = A+ Simazine, M = A+ Simetryn

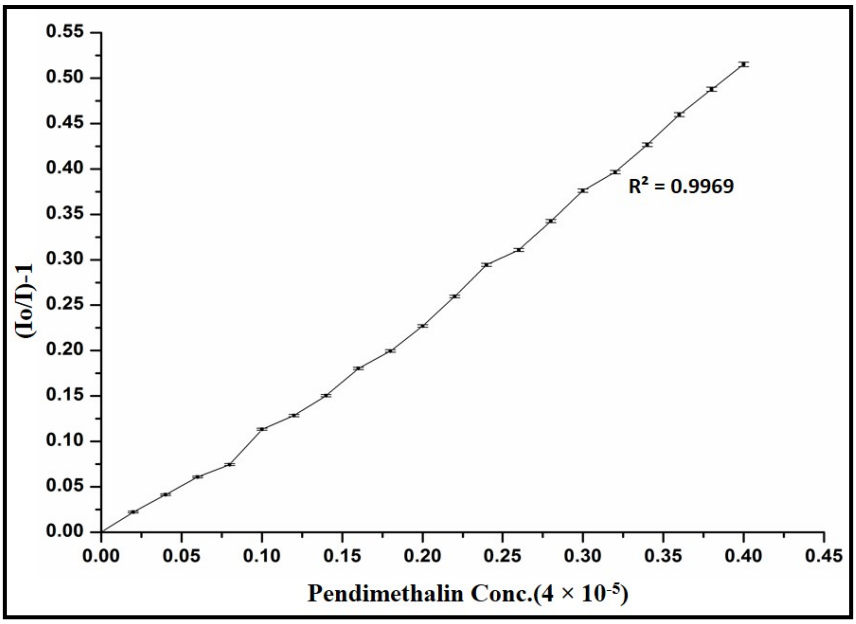

Fig. S3 Stern-Volmer plot for quenching of BDO (4×10^{-5} mol L^{-1}) in methanol by PM

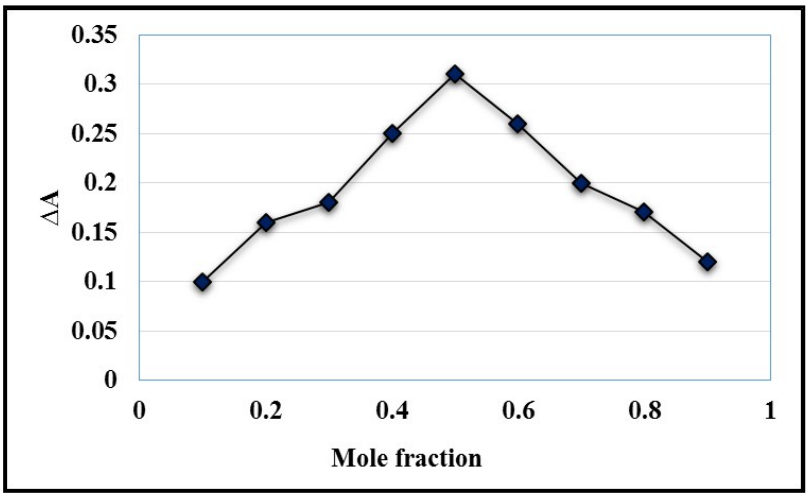

Fig. S4 Job's plot for the BDO and PM

8. Determination of Quantum yield

The quantum yield was determined by the comparative method:

$$\Phi = \Phi_{std} \frac{(F \times A_{std} \times \eta)}{(F_{std} \times A \times \eta_{std})}$$

Here, F and F_{std} are the areas under the fluorescence emission curves of the PM complex with BDO and the standard BDO, respectively. η and η_{std} are the refractive indices of methanol used for the sample and standard, respectively. A and A_{std} are the relative absorbance of the sample and standard at the absorption wavelength, respectively. The sample and the standard both were excited at the same relevant wavelength. Using emission spectra of DC (standard fluorophore) the quantum yield of BDO (fluoroionophore) was determined.

9. Computational details

A host-guest complex of BDO was optimized at the density functional level (DFT) of theory using B3LYP/6-31G* in Gaussian09 [2]. The optimized structures were employed as the starting host and guest conformations for docking in Hex 8.0.0 software [3]. The program utilizes spherical polar Fourier (SPF) basis functions and grid sampling to develop functions for 1D, 3D and 5D orientations and implements fast Fourier transformation (FFT) rotational correlation over angular terms in a constrained search space to extract the best pairwise interactions between the host and guest molecules.

The best docked pose from each of the top ten clusters was retrieved from 2000 orientations through Hex docking. The lowest energy pose with the lowest ΔE_{total} (energy term in Hex software) was provided as the input for molecular dynamics (MD) simulation using the Desmond program version 2.0 (academic version) [4, 5]. The simple point charge (SPC) solvation method was considered, and OPLS-2005 force field parameters were assigned to

define the atom type of the molecular system [6]. The simulation box was centered in the host-guest complex with orthorhombic dimensions (10 Å × 10 Å × 10 Å), followed by the addition of SPC water molecules, and the complete system was then neutralized by adding Na^+ and Cl^- counter ions. After the solvent environment construction, which contained 4033 atoms, the system was energy-minimized and pre-equilibrated in a series of restrained steps to relax the system without deviating much from the initial coordinates.

The MD simulation was executed with a constant volume and shape ensemble (NVT) with a Nose-Hoover thermostat having a relaxation time of 1 ps at 300 K for a duration of 10 ns. A short-range cut off distance of 9.0 Å was selected, and electrostatic interactions were treated using the Smooth Particle Mesh Ewald (PME) method [7] with a 10-9 tolerance limit. The structural changes and dynamic behavior of the complex were investigated by analyzing the change in molecular properties, such as intramolecular hydrogen bonds, gyration radius and RMSD, as a function of time.

10. NMR titration of the host-guest complex

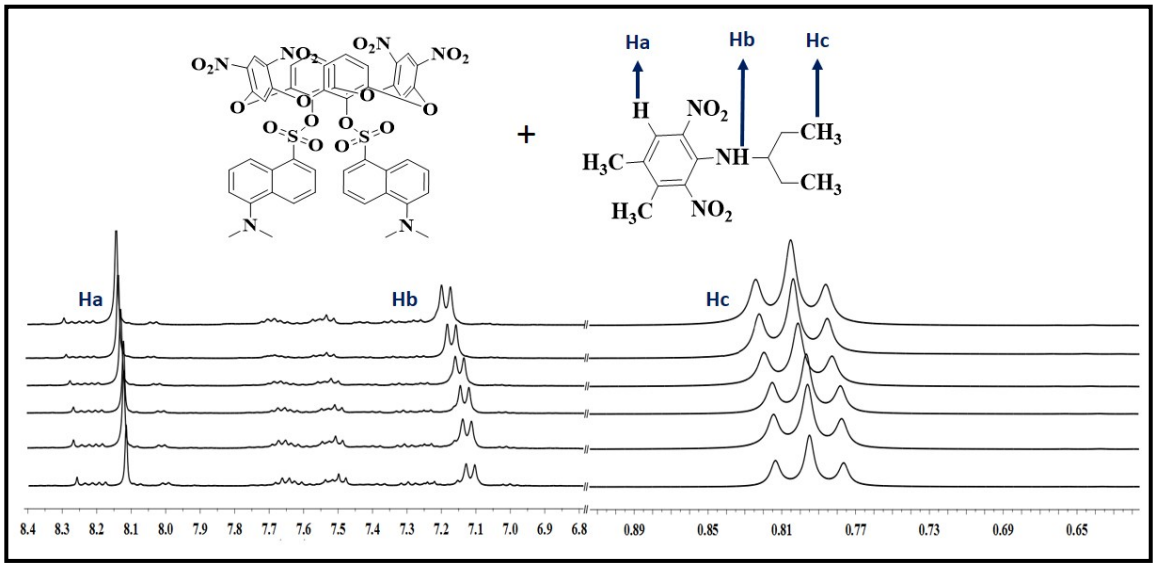

Figure S5. ^{1}H NMR spectra (DMSO-d_6, 500 MHz, 298 K) of PM at a concentration of 4.0 mM with different concentrations of BDO: (a) 4.0 mM, (b) 8.0 mM, (c) 15.0 mM, (d) 25.0 mM, (e) 35.0 mM, (f) 40.0 mM. With increasing concentrations of host BDO, the PM aromatic **Ha** proton,-NH **Hb** proton and methyl **Hc** proton, undergo downfield shift of 0.030, 0.060 and 0.012 ppm respectively. NMR titration indicate PM is well integrated with the oxacalixarene moiety.

11. Docked complex of BDO and PM

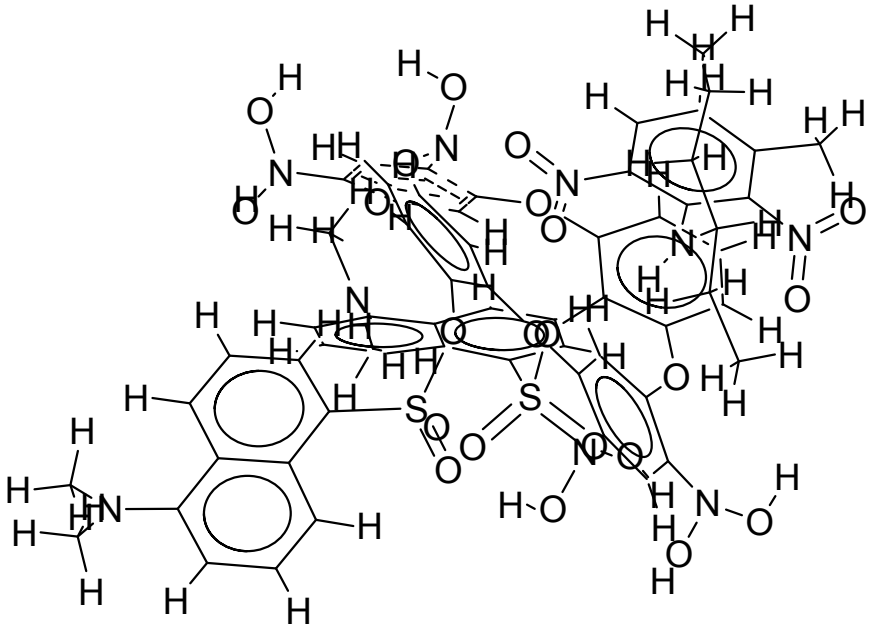

Fig. S6Docked complex of BDO and PM

12. Comparison of present fluorescent probe with various previously reported PM determination methods, Table S1

Methods	Detection limit	Reference
Square wave voltammetry Method	1.92×10^{-8} (4.88 μg L^{-1})	**8**
Adsorptive Stripping Voltammetry	3.34×10^{-9} (0.94 μg L^{-1})	**9**
Enzyme-linked immunosorbent assays	3.02×10^{-9} (0.85 μg L^{-1})	**10**
Differential pulse voltammetry	4.10×10^{-7} (115.3 μg L^{-1})	**11**
Liquid–liquid extraction	1.78×10^{-8} (5.0 μg L^{-1})	**12**
Ultrasonic extraction	1.07×10^{-9} (0.3 μg L^{-1})	**13**
Spectrofluorimetric Method	3.81×10^{-9}(1.07 μg L^{-1})	**This Work**

13. XYZ coordinates of pendimethalin-BDO Complex

Total Atoms 155

```
C   2.4800   0.0690   0.3540
C   1.0870   0.1740   0.2790
C   0.4930   1.2080  -0.4730
C   1.3130   2.1740  -1.1260
C   2.7410   2.0860  -1.0410
C   3.2890   0.9970  -0.3150
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C 0.7370 3.2230 -1.8820
C 1.5420 4.1330 -2.5800
C 2.9390 4.0490 -2.4900
C 3.5540 3.0680 -1.6900
S 5.3290 3.1200 -1.5410
N -0.8770 1.2030 -0.5560
C -1.6760 1.6610 0.5480
C -1.5280 0.6770 -1.7270
O 7.9680 4.5650 -4.4410
O 6.0700 4.6140 -2.0280
C 9.0270 4.1350 -1.6260
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C 6.4010 6.2450 1.2710
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C 9.9630 3.3400 -2.3260
C 4.2160 7.8050 -5.9190
C 3.8470 7.4990 -4.5850
C 4.8610 7.0940 -3.6810
O 4.5280 7.0740 -2.3560
C 5.5530 7.7030 -6.3740
C 6.0250 5.5780 -1.0510
C 10.2340 6.7830 -6.2970
C 6.1780 6.8880 -4.1520
C 6.5280 7.1740 -5.4910
O 7.7920 7.0660 -5.9930
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O 7.7470 4.5490 0.4140
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14. XYZ coordinates of Simazine-BDO Complex

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Total Atoms 145
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H  2.7860  5.8550 -8.8980
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N  8.9400  8.1770 -3.4780
C  8.7400  7.9200 -2.2020
N  7.8160  8.4930 -1.4630
C  7.0660  9.3780 -2.0930
N  7.1740  9.7150 -3.3630
C  8.1310  9.0790 -4.0030
Cl 8.3470  9.4560 -5.6750
N  9.5070  7.0070 -1.5350
C  5.9760 10.0970 -1.3500
C 10.6240  6.1920 -2.0690
C 11.3630  5.1790 -1.0330
N  5.1280 11.0850 -2.0240
C  4.0400 11.8480 -1.4110
H  9.2760  6.8850 -0.5710
H  6.0900  9.6580 -0.3590
H  5.5010 10.1880 -0.3730
H 10.5580  6.5940 -3.0750
H 11.0660  6.1460 -3.0920
H 11.8530  5.0630 -1.9790
H 12.1220  4.4260 -0.8150
H 10.6630  5.5490 -0.2890
H  5.3510 11.2210 -3.0060
H  3.7470 11.7520 -0.3650
H  3.3050 12.6010 -1.6960
H  3.8120 12.3690 -2.3420
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