SUPPORTING INFORMATION

O-Vanillin scaffold as selective chemosensor of PO_4^{3-} and the application of neural network based soft computing to predict machine learning outcome

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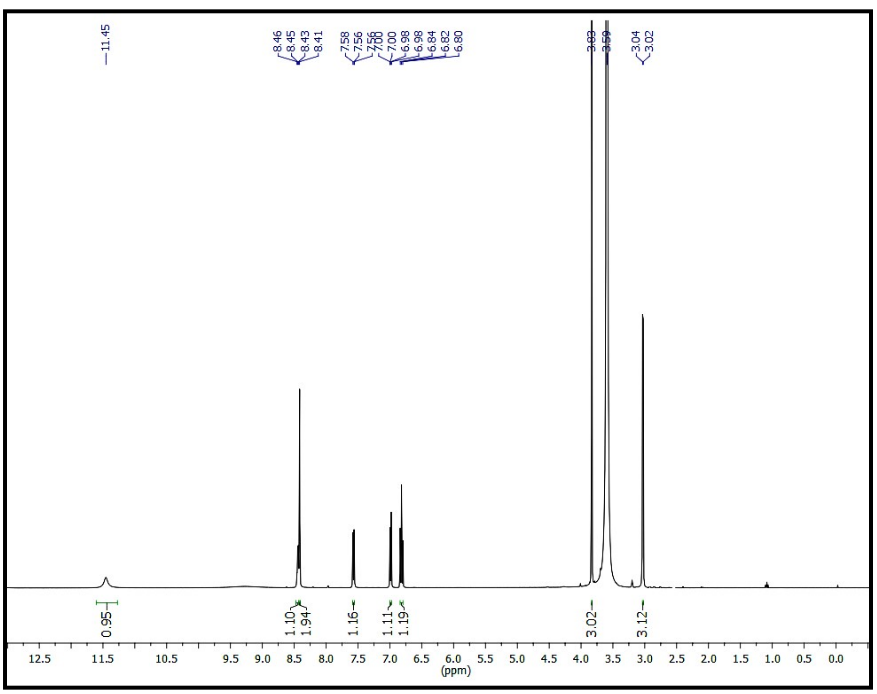


Fig. S1 ^{1}H NMR spectra of VCOH in DMSO-d^6.

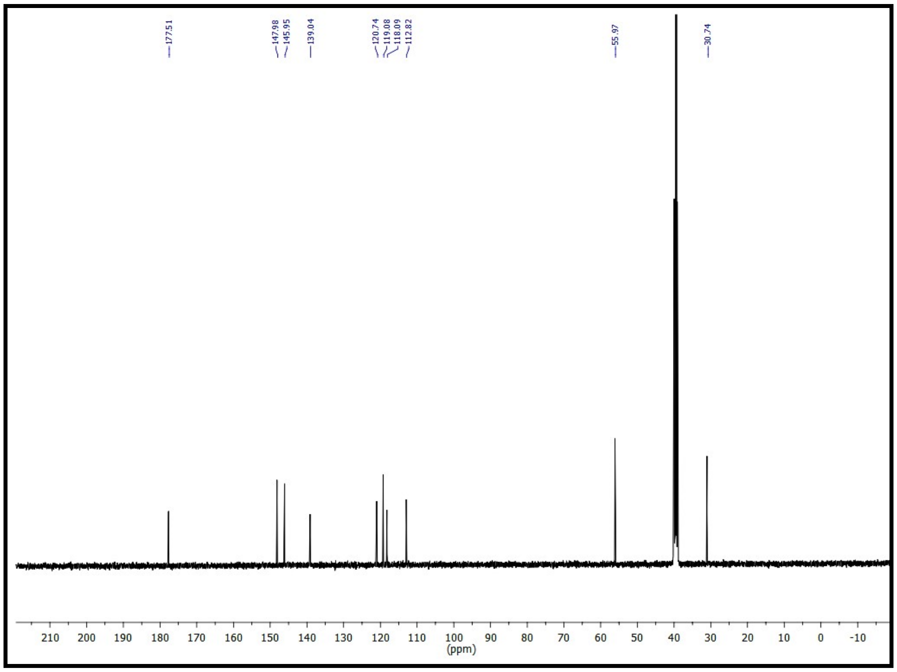


Fig. S2 ^{13}C NMR spectra of VCOH in DMSO-d^6.

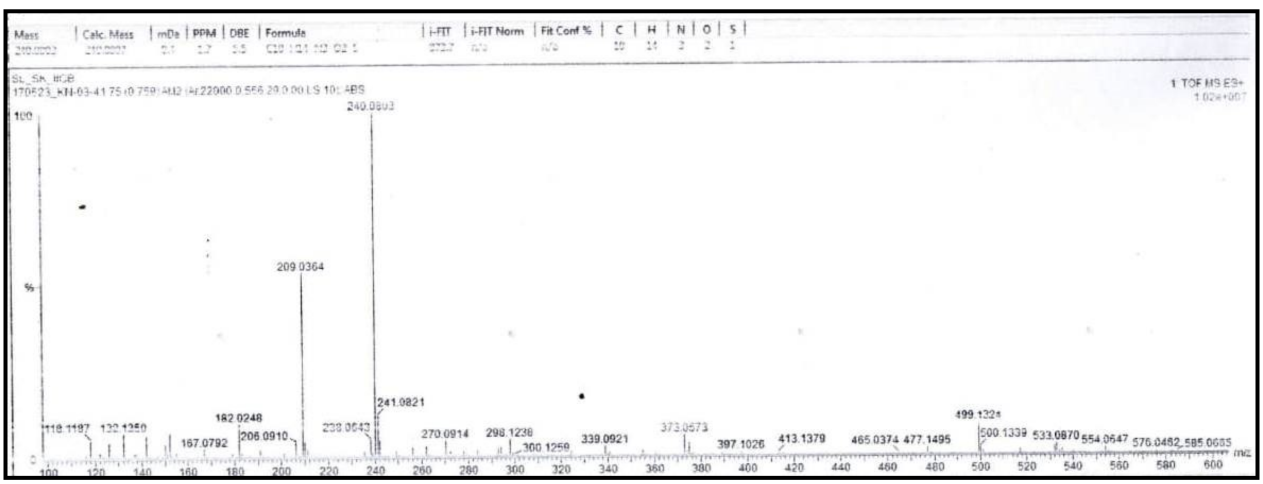


Fig. S3 High resolution mass spectra of VCOH.

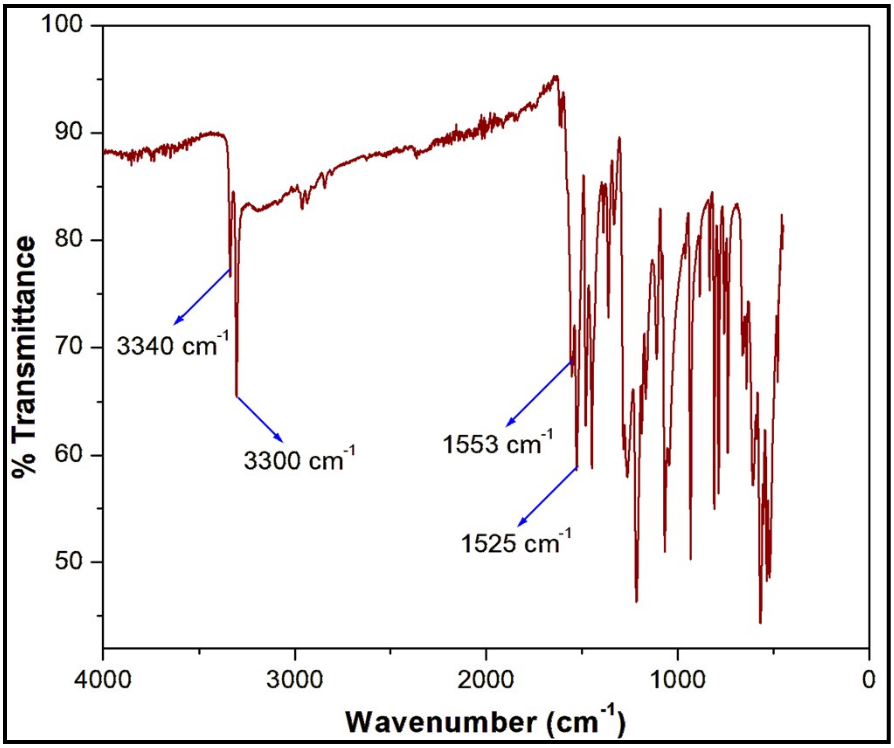


Fig. S4 IR spectra of VCOH showing peaks at 3340 cm^{-1}, 3340 cm^{-1}, 1553cm^{-1} and 1525 cm^{-1} for O–H, N–H, C=N and C=S bond respectively.

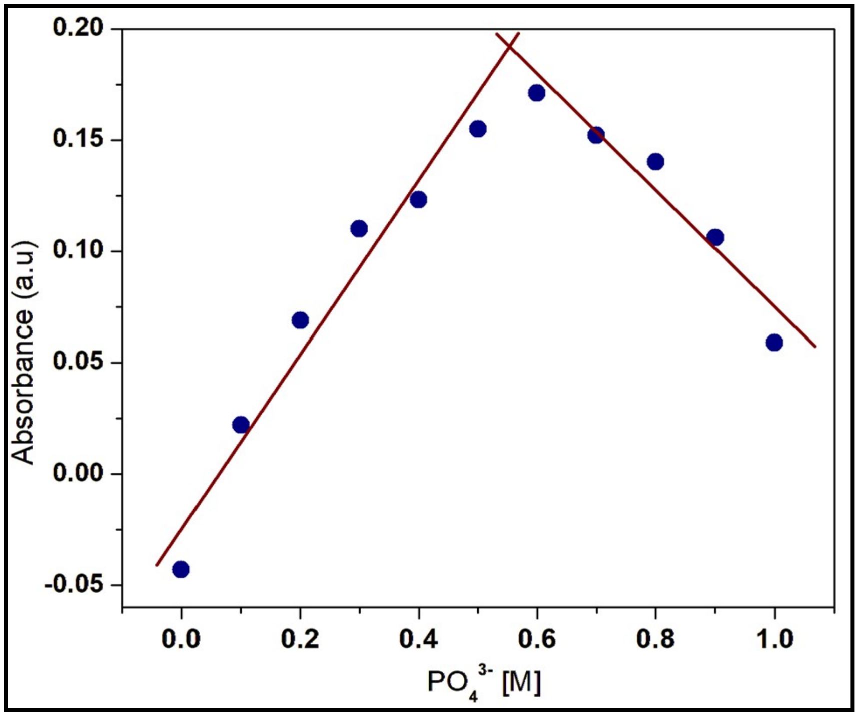


Fig. S5 Job's plot of VCOH in presence of PO_4^{3-} using continuous variation method, indicating the 1:1 stoichiometric interaction between VCOH and PO_4^{3-} ion.

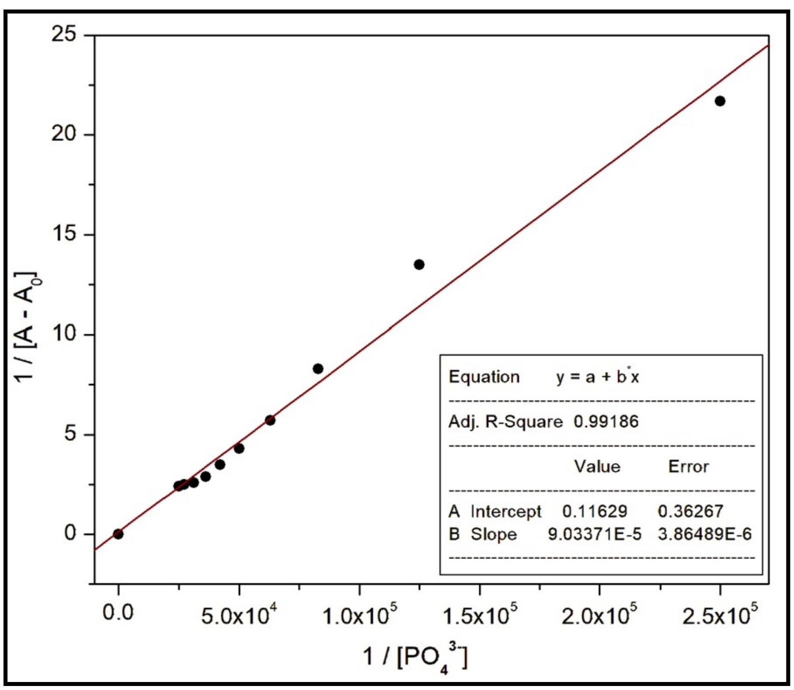


Fig. S6 Benesi-Hildebrand plot of absorbance intensity at 392 nm wavelength of PNOH with increasing concentration of PO_4^{3-} ion.

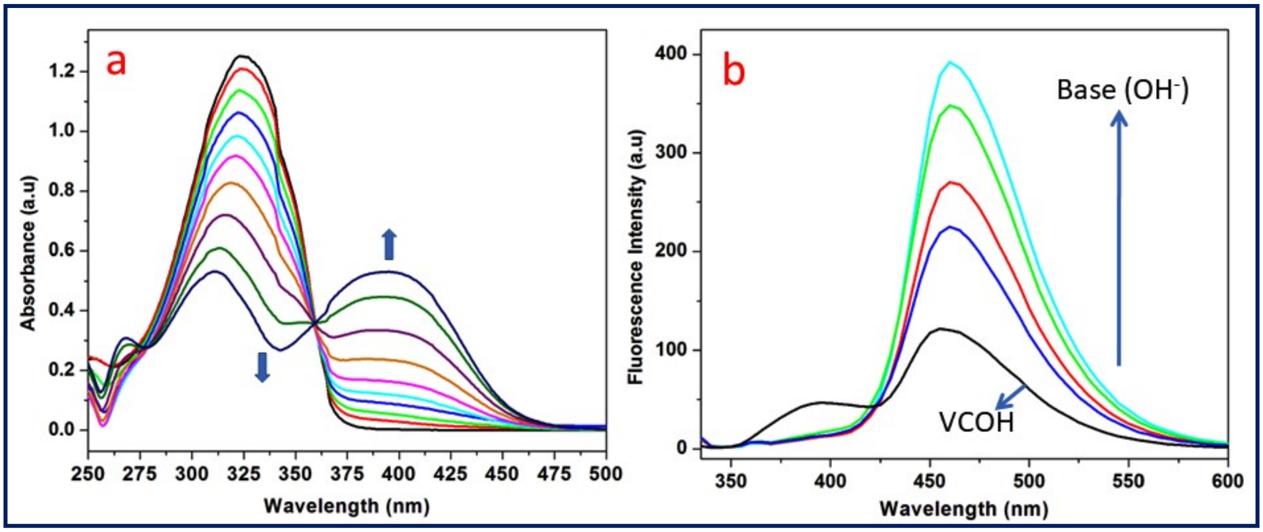


Fig. S7 (a) UV-Vis absorption and (b) emission spectra of VCOH in presence of increasing concentration (0 – 8.0 mM) of base (NaOH).

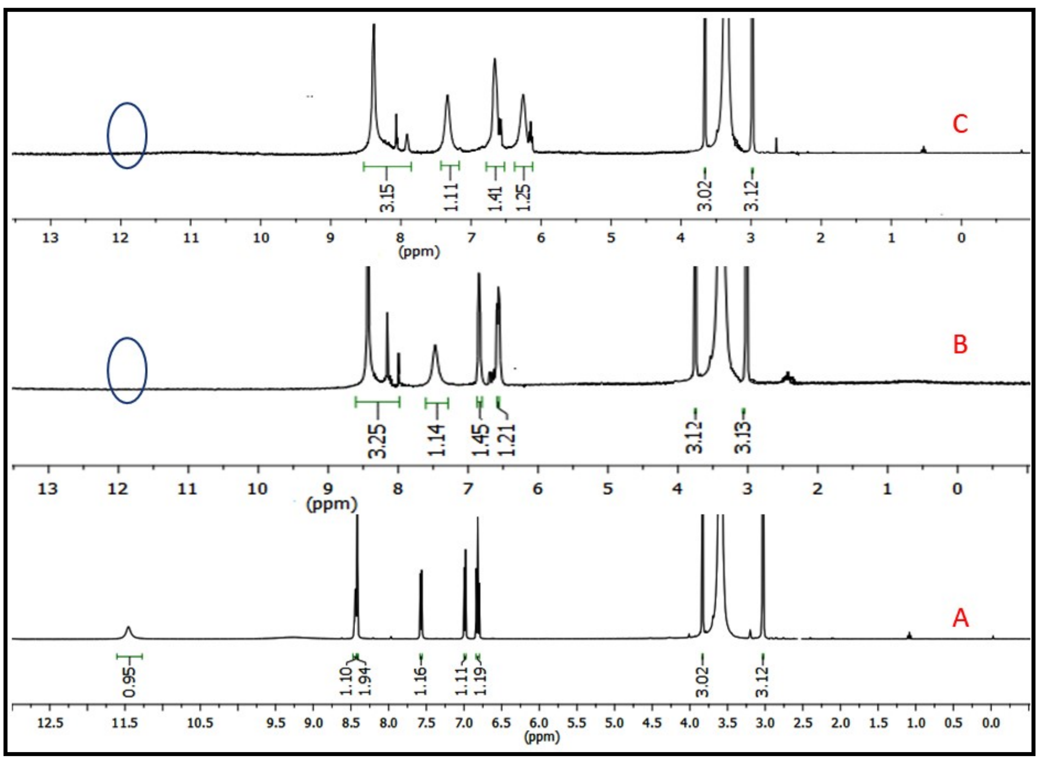


Fig. S8 ^{1}H NMR spectra in DMSO-$d_6$of (A) VCOH, (B) VCOH in presence of 1 equivalent $PO_4^{3-}$and (C) VCOH in presence of 2 equivalent PO_4^{3-}.

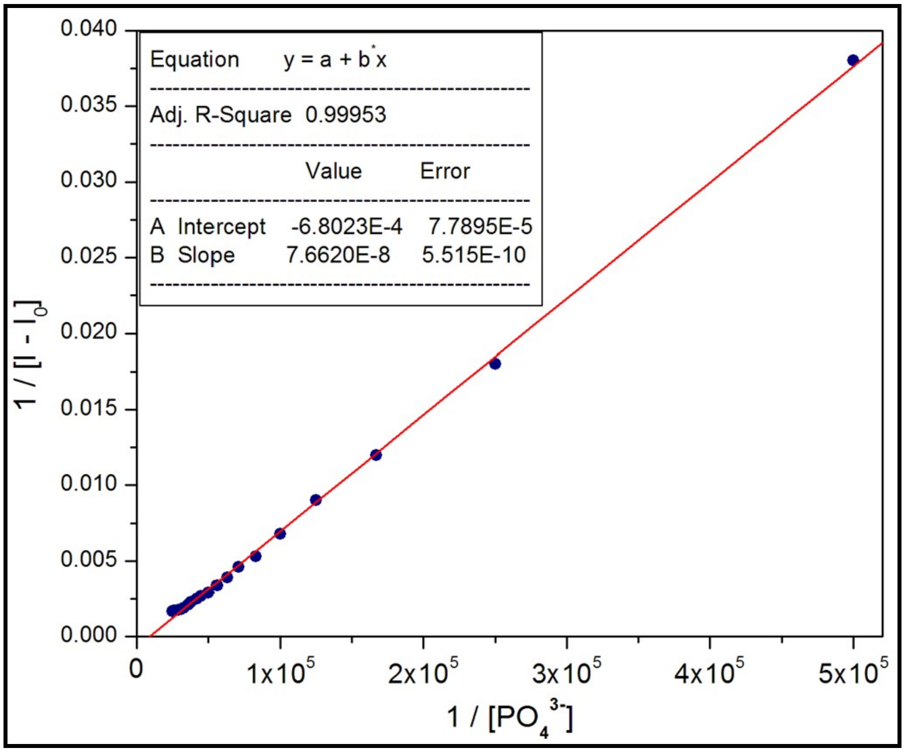


Fig. S9 Benesi-Hildebrand plot of emission intensity at 462 nm wavelength of PNOH with increasing concentration of PO_4^{3-} ion.

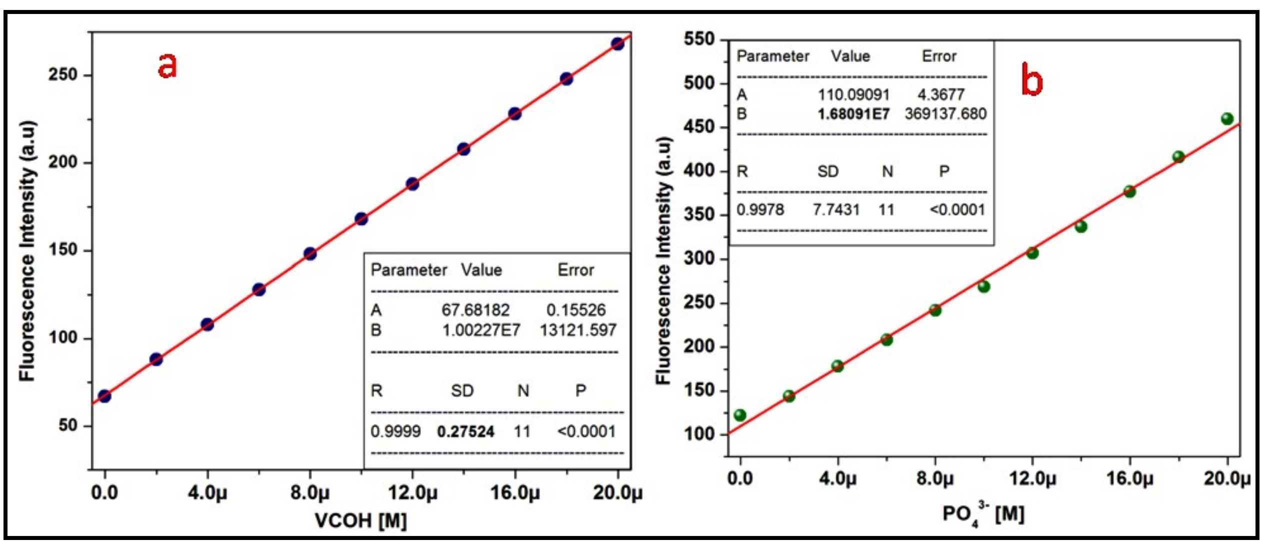


Fig. S10 (a) Plot of fluorescence intensity *vs*. concentration of VCOH for measuring standard deviation (σ); (b) plot of fluorescence intensity *vs*. concentration of PO_4^{3-} for measuring slope (k), of LOD experiment [LOD = (3 x 0.275)/1.68091 x 10^7 M = 0.49nM].

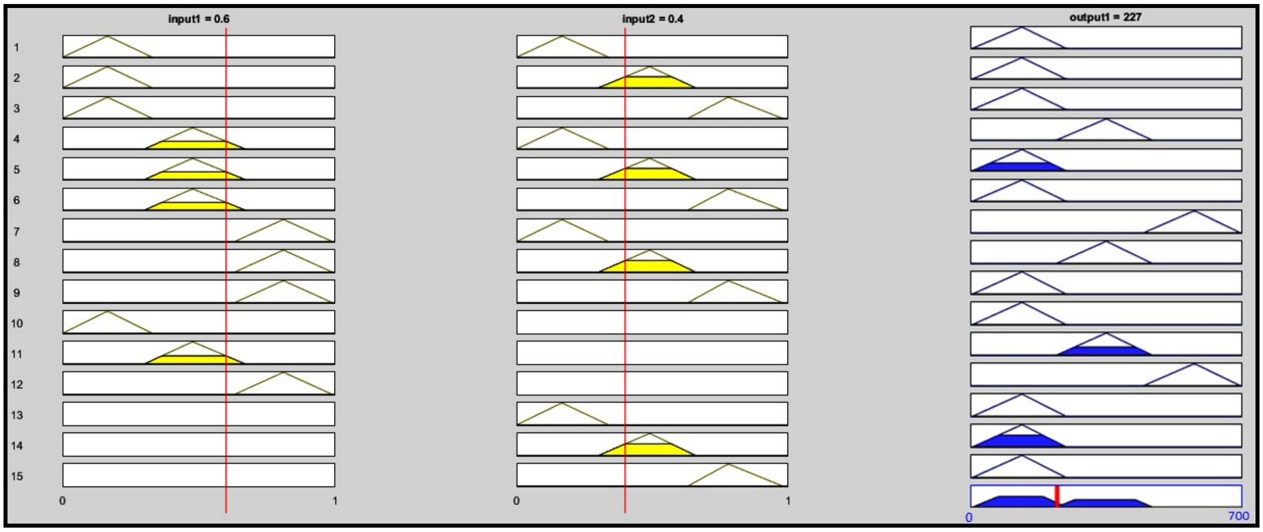


Fig. S11 Mamdani rule viewer for VCOH.

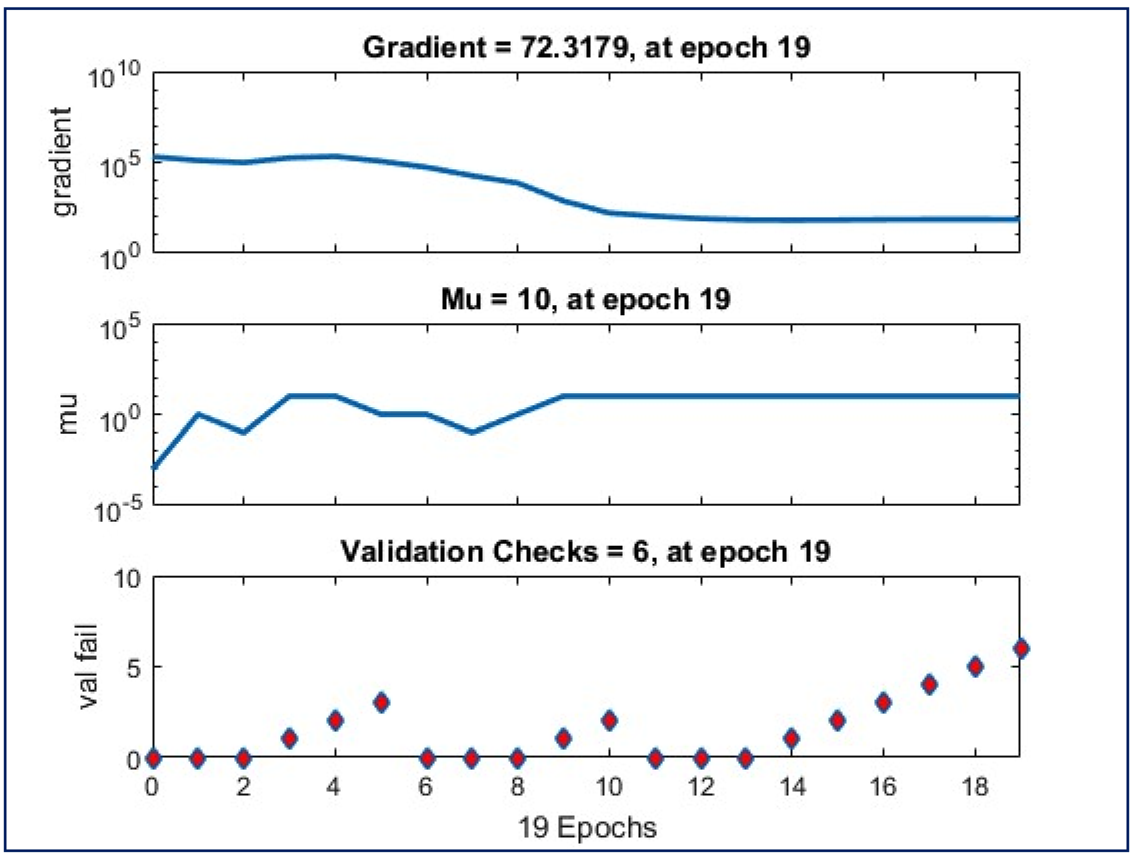


Fig. S12 Training state of the ANN model of VCOH (monitoring wavelength at 459 nm) up to epoch 19.

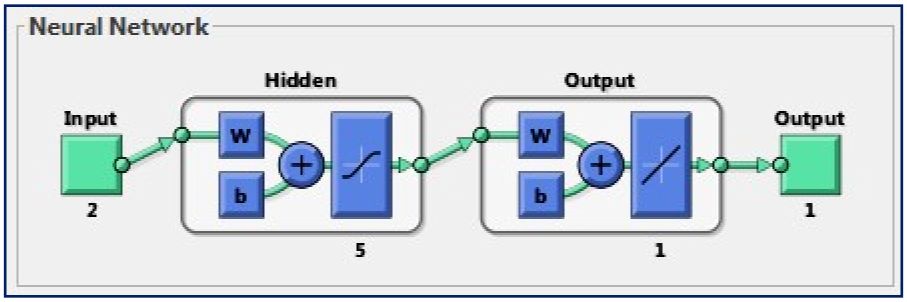


Fig. S13 Artificial neural network model consisting of 2 inputs, 5 hidden layers, and 1 output.

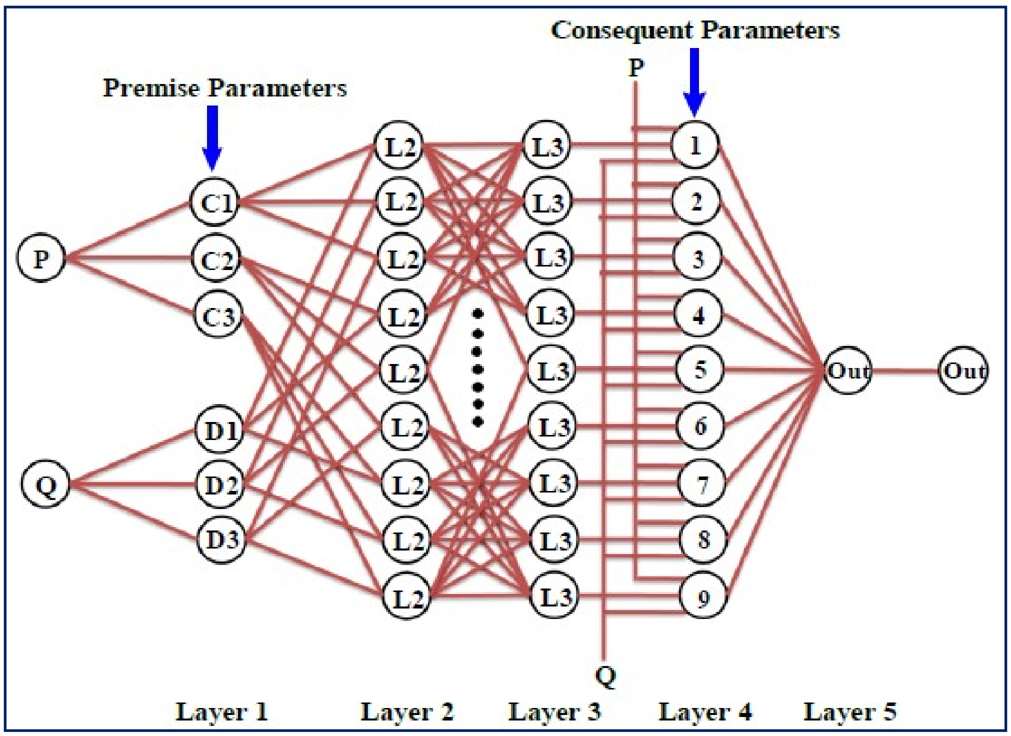


Fig. S14 Schematic sketch of ANFIS network comprising two inputs, five layers, and one output.

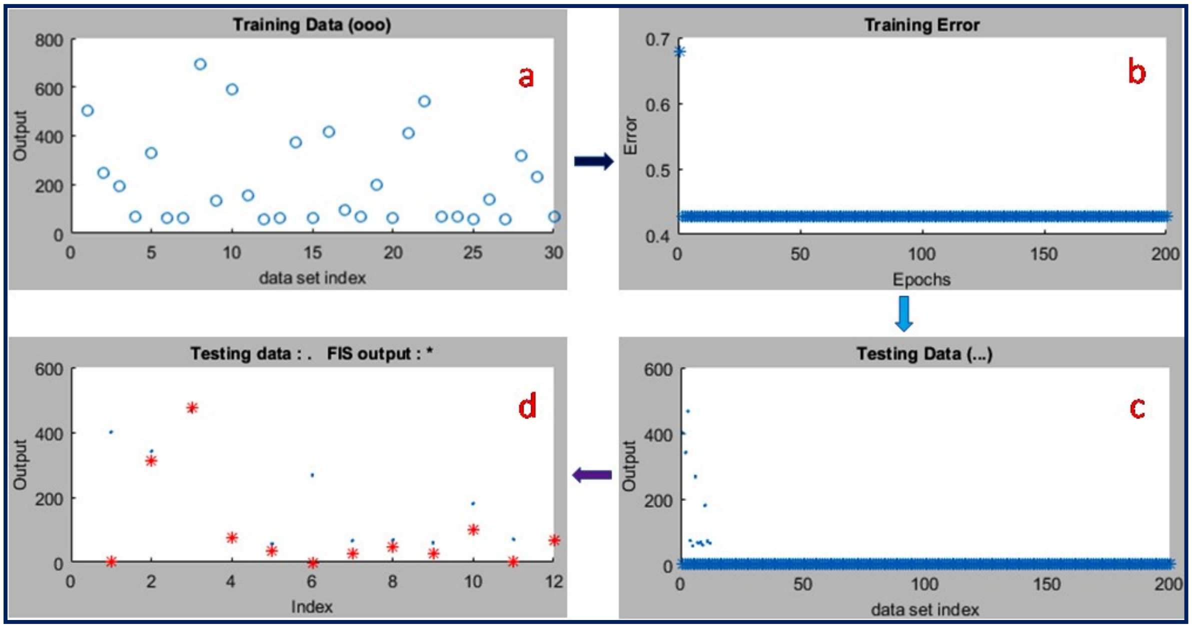


Fig. S15 (a) Data set to train the ANFIS network. (b) Root mean square error (RMSE) minimization up to 200 epochs. (c) Data for testing the accuracy of the network output. (d) Combination of testing data and the FIS output.

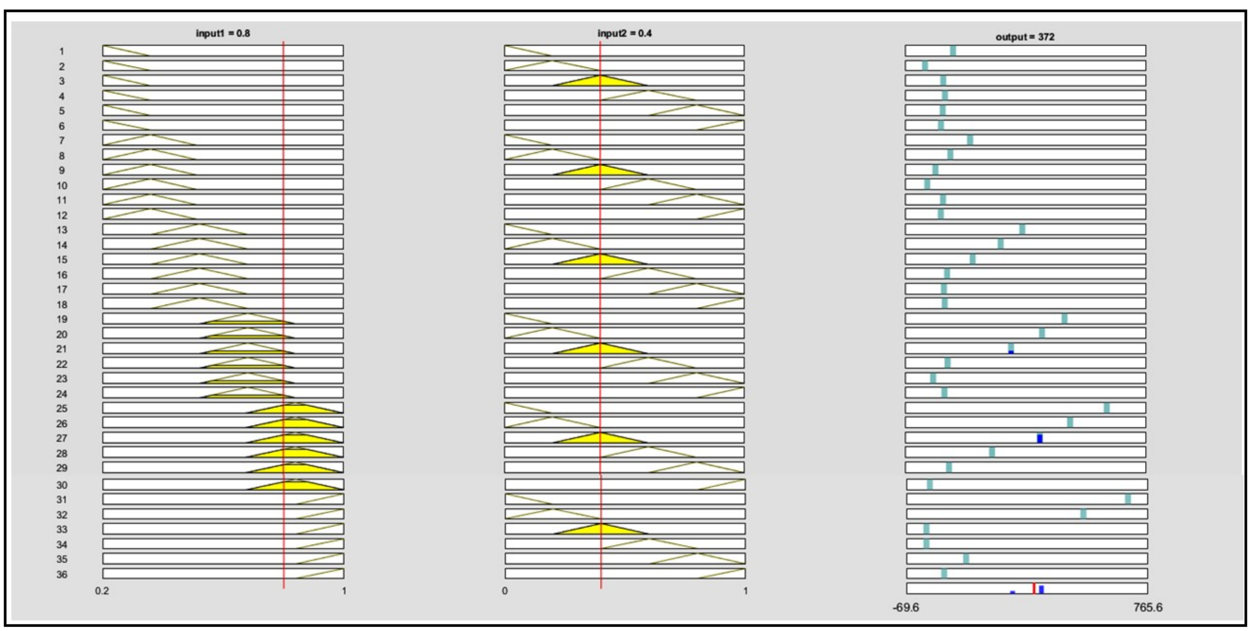


Fig. S16 Sugeno rule viewer for VCOH (monitoring wavelength at 459 nm).

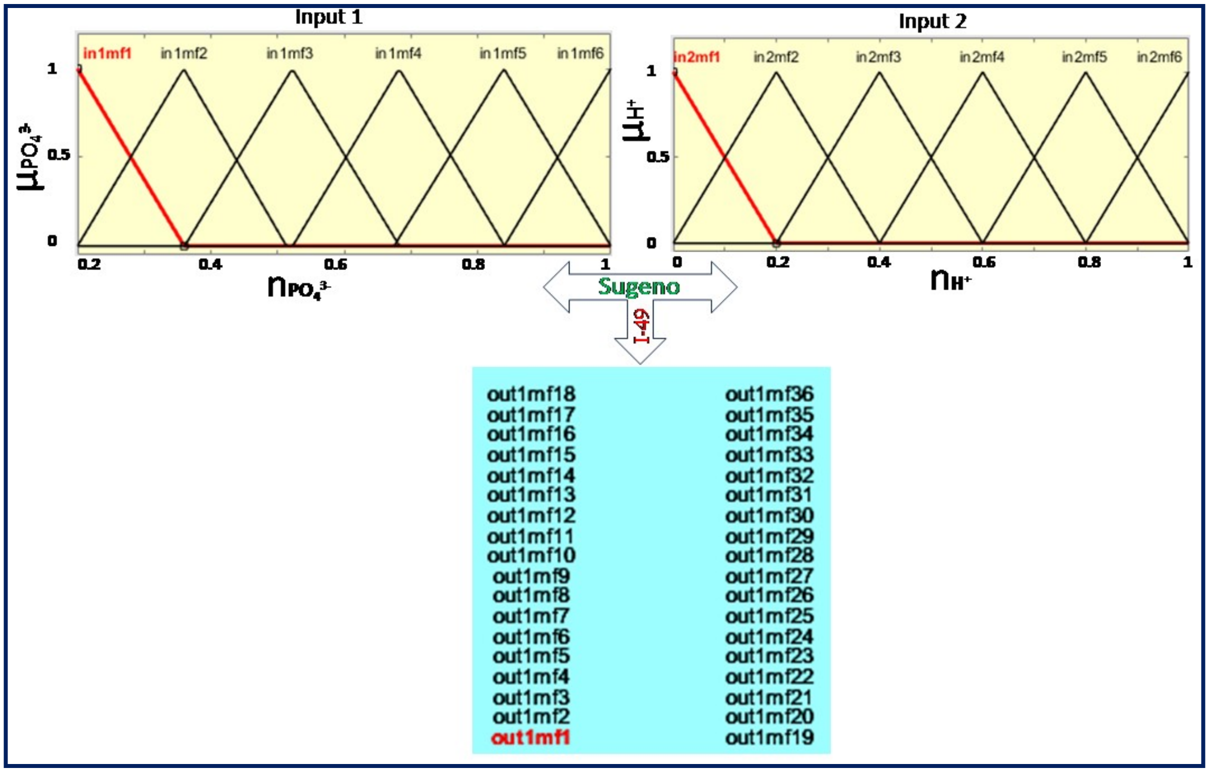
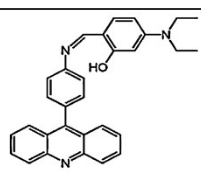


Fig. S17 Schematic diagram of ANFIS on the basis of Sugeno's method (monitoring at 459 nm) maintaining 36 rules.

Table S1 Comparative Study of VCOH with other reported PO_4^{3-} ion sensors.

Sl. No.	probe	No. of steps for synthesis	Method for PO_4^{-3} detection	Time response	LOD	Binding Constant (k) (M^{-1})	On-site application (paper strips)	$\lambda_{ex}/\lambda_{em}$ (nm)	Ref.
1		3	'turn-off' response through decomple-xation of metal ion	NA	2.63 μM	NA	NA	430/480	37

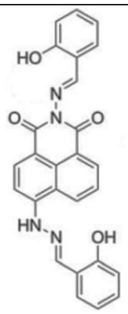
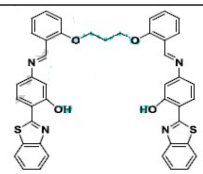
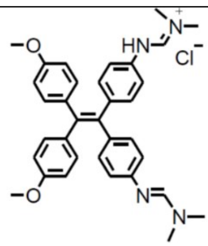
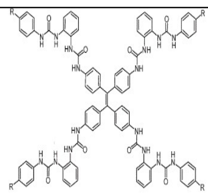
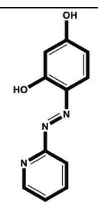
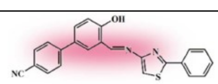
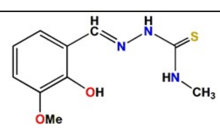
2		2	'turn-on' response through decomple-xation of metal ion	NA	1.7 µM	NA	Yes	440/531	39
3		3	'turn-on' response through decomple-xation of metal ion	NA	31.6 µM	NA	Yes	360/422	40
4		3	AIE based 'turn-on' response	NA	--	2.36 x 10^4	NA	400/502	41
5		2	ACIE based 'turn-on' response	NA	--	NA	NA	429/500	42
6		2	'turn-on' response through decomple xation of metal ion	NA	0.11 µM	1.3 x 10^5	NA	NA	46
7		2	Colorimet ric by metal complex	NA	18.6 µM	NA	NA	420/580	47
8		1	**Direct 'turn-on' response through deproton ation**	**Instant ('zero wait' response)**	0.49 nM	8.9 x 10^3	Yes	325/459	**Present work**

Table S2 Different values of emission intensity of VCOH on the ratiometric variation of PO_4^{3-} and H^+.

No. of obs.	Equivalents of PO_4^{3-}	Equivalents of H^+	Emission intensity at 459 nm
1.	1	0.4	401
2.	0.7	0.4	341
3.	0.8	0.2	467
4.	0.6	0.6	73
5.	0.7	0.8	57
6.	1	0.6	268
7.	0.7	0	503
8.	0.5	0.2	246
9.	0.8	0.6	193
10.	0.4	0.4	68
11.	0.6	0.2	331
12.	0.2	0.4	63
13.	0.5	0.8	65
14.	1	0	696
15.	0.4	0.2	131
16.	0.8	0	592
17.	0.5	0.4	153
18.	0.2	1	55
19.	0.4	0.8	63
20.	0.8	0.4	372
21.	1	1	61
22.	0.7	0.2	419
23.	0.2	0	97
24.	0.5	0.6	70
25.	0.4	0	201
26.	0.2	0.8	61
27.	0.6	0	409
28.	1	0.2	542
29.	0.5	1	67
30.	0.8	0.8	69
31.	0.4	1	58
32.	1	0.8	137
33.	0.7	1	59
34.	0.5	0	319

35.	0.6	0.4	229
36.	0.2	0.6	69
37.	0.8	1	67
38.	0.6	0.8	68
39	0.4	0.6	60
40.	0.7	0.6	181
41.	0.2	0.2	71
42.	0.6	1	66

Table S3 Rules for the fuzzy logic system of VCOH where input 1 = PO_4^{3-}, input 2 = H^+, and output = emission intensity at 459 nm. The rules encompass the following statements-

1. If (input1 is Low) and (input2 is Low) then (output1 is Low) (1)
2. If (input1 is Low) and (input2 is Medium) then (output1 is Low) (1)
3. If (input1 is Low) and (input2 is High) then (output1 is Low) (1)
4. If (input1 is Medium) and (input2 is Low) then (output1 is Medium) (1)
5. If (input1 is Medium) and (input2 is Medium) then (output1 is Low) (1)
6. If (input1 is Medium) and (input2 is High) then (output1 is Low) (1)
7. If (input1 is High) and (input2 is Low) then (output1 is High) (1)
8. If (input1 is High) and (input2 is Medium) then (output1 is Medium) (1)
9. If (input1 is High) and (input2 is High) then (output1 is Low) (1)
10. If (input1 is Low) then (output1 is Low) (1)
11. If (input1 is Medium) then (output1 is Medium) (1)
12. If (input1 is High) then (output1 is High) (1)
13. If (input2 is Low) then (output1 is Low) (1)
14. If (input2 is Medium) then (output1 is Low) (1)
15. If (input2 is High) then (output1 is Low) (1)

Table S4 Rules for the ANFIS (based on Sugeno's method) by taking PO_4^{3-} as input 1 and H^+ as input 2, whereas emission intensity at 678 nm as the output. The rules encompass the following statements-

1. If (input1 is in1mf1) and (input2 is in2mf1) then (output is out1mf1) (1)
2. If (input1 is in1mf1) and (input2 is in2mf2) then (output is out1mf2) (1)
3. If (input1 is in1mf1) and (input2 is in2mf3) then (output is out1mf3) (1)
4. If (input1 is in1mf1) and (input2 is in2mf4) then (output is out1mf4) (1)
5. If (input1 is in1mf1) and (input2 is in2mf5) then (output is out1mf5) (1)
6. If (input1 is in1mf1) and (input2 is in2mf6) then (output is out1mf6) (1)
7. If (input1 is in1mf2) and (input2 is in2mf1) then (output is out1mf7) (1)
8. If (input1 is in1mf2) and (input2 is in2mf2) then (output is out1mf8) (1)
9. If (input1 is in1mf2) and (input2 is in2mf3) then (output is out1mf9) (1)
10. If (input1 is in1mf2) and (input2 is in2mf4) then (output is out1mf10) (1)
11. If (input1 is in1mf2) and (input2 is in2mf5) then (output is out1mf11) (1)
12. If (input1 is in1mf2) and (input2 is in2mf6) then (output is out1mf12) (1)
13. If (input1 is in1mf3) and (input2 is in2mf1) then (output is out1mf13) (1)
14. If (input1 is in1mf3) and (input2 is in2mf2) then (output is out1mf14) (1)
15. If (input1 is in1mf3) and (input2 is in2mf3) then (output is out1mf15) (1)
16. If (input1 is in1mf3) and (input2 is in2mf4) then (output is out1mf16) (1)
17. If (input1 is in1mf3) and (input2 is in2mf5) then (output is out1mf17) (1)
18. If (input1 is in1mf3) and (input2 is in2mf6) then (output is out1mf18) (1)
19. If (input1 is in1mf4) and (input2 is in2mf1) then (output is out1mf19) (1)
20. If (input1 is in1mf4) and (input2 is in2mf2) then (output is out1mf20) (1)
21. If (input1 is in1mf4) and (input2 is in2mf3) then (output is out1mf21) (1)
22. If (input1 is in1mf4) and (input2 is in2mf4) then (output is out1mf22) (1)
23. If (input1 is in1mf4) and (input2 is in2mf5) then (output is out1mf23) (1)
24. If (input1 is in1mf4) and (input2 is in2mf6) then (output is out1mf24) (1)
25. If (input1 is in1mf5) and (input2 is in2mf1) then (output is out1mf25) (1)
26. If (input1 is in1mf5) and (input2 is in2mf2) then (output is out1mf26) (1)
27. If (input1 is in1mf5) and (input2 is in2mf3) then (output is out1mf27) (1)
28. If (input1 is in1mf5) and (input2 is in2mf4) then (output is out1mf28) (1)
29. If (input1 is in1mf5) and (input2 is in2mf5) then (output is out1mf29) (1)
30. If (input1 is in1mf5) and (input2 is in2mf6) then (output is out1mf30) (1)
31. If (input1 is in1mf6) and (input2 is in2mf1) then (output is out1mf31) (1)
32. If (input1 is in1mf6) and (input2 is in2mf2) then (output is out1mf32) (1)
33. If (input1 is in1mf6) and (input2 is in2mf3) then (output is out1mf33) (1)
34. If (input1 is in1mf6) and (input2 is in2mf4) then (output is out1mf34) (1)
35. If (input1 is in1mf6) and (input2 is in2mf5) then (output is out1mf35) (1)
36. If (input1 is in1mf6) and (input2 is in2mf6) then (output is out1mf36) (1)

Experimental section

Artificial neural network (ANN)

An artificial neural network is a network that is modeled after the central nervous system of animals, primarily the brain. Artificial neural networks (ANNs) are commonly used to predict functions that may depend on numerous unknown inputs. We used feed-forward neural networks (FNN) in this study because our system is static, rather than recurrent neural networks (RNN). FNN is a simple and convenient type of network where information flows in one direction - from input nodes, through hidden nodes, and finally to output nodes. For a deeper understanding and better forecasting of the system, we implemented an advanced ANN-FF network, known for its high efficiency in forecasting static systems.

A model of an artificial neural network that has two inputs, five hidden layers, and one output. In ANN-FF, experimental data is used to approximate the input-output relation as a function. The network diagram for the ANN-FF system is available in Fig. S13. When the hidden layer has enough neurons and consistent data is used, it can solve multidimensional mapping problems effectively. A neural network is necessary to map data set inputs to targets. Therefore, a numerical value is assigned to each pattern, such as 1, 2, 3, 4, and so on.

In this study, a neural network for function fitting was coded in MATLAB 2018. The network input data is defined by the target output data. Table S2 shows the emission intensity as output resulting from 42 combinations of two inputs: PO_4^{3-} and H^+. The 42×2 matrix represents the input data of 42 samples with 2 inputs, while the 42×1 matrix represents the output data (at 459 nm) of one element. The 42 samples have been separated into 3 distinct sets of data. During training, 70% of the data is used and the network is adjusted based on its errors. The learning algorithm was optimized and the number of neurons in the hidden layer was adjusted. 15% data are employed to compute the network generalization and to halt training. When generalization stops improving, data validation takes place. The remaining 15% of data gives an independent estimate of the network performance during and after the training, called testing data (Fig. 9a).

Adaptive neuro-fuzzy inference system (ANFIS)

The network framework of the ANFIS is shown in Fig. S14. The network has five connected layers (excluding input) for two input dimensions: P and Q. P has three fuzzy sets (C1C2C3) and Q has three fuzzy sets (D1D2D3). We have selected A number of inputs and B number of fuzzy sets to represent each input. This implies A×B nodes in Layer 1. In Layer 2, each input node's membership function output is connected to all other nodes, resulting in a total of B^A nodes. Layers 3 and 4 have the same number of nodes as Layer 2. Layer 5 represents the output of the network with only one node. When each input is considered a node, the total number of nodes in the architecture is A + A×B + 3×B^A + 1. In ANFIS, only the membership function parameters in Layer 1 and input weights in Layer 4 need to be trained for prediction. When using the trimf function with three parameters, Layer 1 requires an assessment of 3×B×A premise parameters, while Layer 4 requires an assessment of A×B^A consequent weight parameters.

The ANFIS structure is tuned using both least-squares estimation and the back propagation algorithm. A fuzzy set A in a universe X is a collection of ordered pairs of generic elements and its membership function μA(x): X → [0, 1], which assigns a number μA(x) to each element x of X. The fuzzy logic controller operates based on fuzzy rules among linguistic variables. These fuzzy rules are represented in the form of conditional statements.

The ANFIS pattern predictor model for flow regime consists of four parts: fuzzification, knowledge base, artificial neural network, and defuzzification blocks (Scheme 3). The inputs to the ANFIS are the PO_4^{3-} and H^+. The binary data is converted into linguistic variables by the fuzzification unit. The knowledge base block receives these inputs. During the training of the neural network using MATLAB 2018a's ANFIS tool, 36 rules were developed. The knowledge base block is linked to the artificial neural network block. A hybrid optimization algorithm is utilized to train the neural network and select the appropriate set of rules for the knowledge base. Training is an important step in selecting a proper rule base for predicting emission intensity values at 459 nm. Once the ANFIS model is assigned a rule base, it can begin making predictions. The trained ANFIS was validated using 15% of the data. The linguistic variables are converted back into numerical data in crisp form by the defuzzification unit using the output of the artificial neural network unit as input.