

Molecular Recognition Meets Microcontroller: Calixarene-Based Fluorescent Sensors for Selective Detection of 2-Nitrobenzaldehyde

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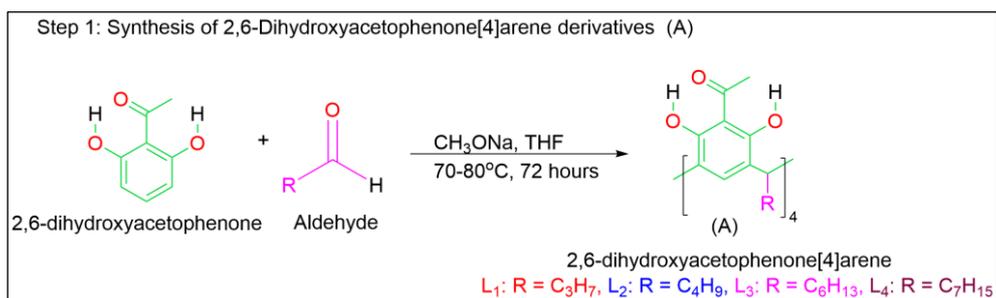
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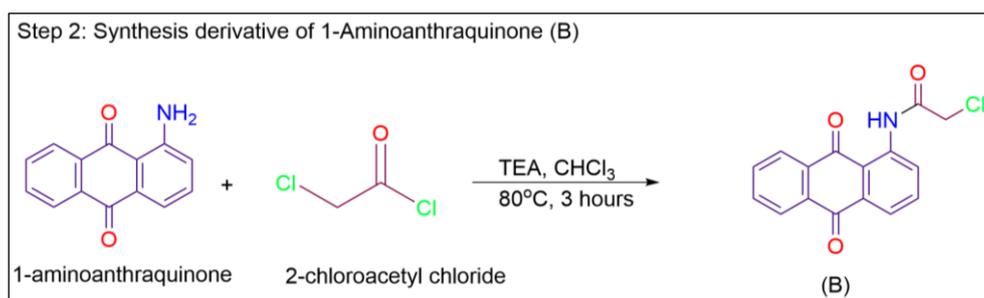
1. Synthesis of 2,6-dihydroxyacetophenone[4]arene (DHP[4]arene)



Scheme 1: Reaction scheme of 2,6-dihydroxyacetophenone[4]arene (DHP[4]arene)

The parental 2,6-dihydroxyacetophenone[4]arene was synthesized by following conventional literature-reported protocol¹. Briefly, 2,6-dihydroxyacetophenone (1 mmol) and aldehyde (1.1 mmol) were dissolved in 10 mL of tetrahydrofuran (THF). Sodium methoxide powder (1.5 mmol) was added, and the reaction mixture was refluxed for 72 hours under continuous stirring. The progress of the reaction was monitored by TLC using an ethyl acetate:hexane (8:2) solvent system. Upon completion, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The resulting crude product was dissolved in 25 mL of methanol, followed by the addition of a few drops of acetic acid. A yellow precipitate formed, which was stirred at 0–5°C for 30 minutes. The solid product was collected by filtration, washed with cold methanol, and purified by column chromatography using an ethyl acetate:hexane solvent system. The final compound was dried at 40–45°C.

2. Synthesis of acetamide derivative of 1-Aminoanthraquinone



Scheme 2: Reaction scheme of acetamide derivative of 1-Aminoanthraquinone

1-aminoanthraquinone (1 mmol) was dissolved in 5 mL of chloroform solvent. 1.2 mmol of trimethylamine was added as a base. Following that, 1.6 mmol of 2-chloroacetyl chloride dropped wise introduced to the reaction mixture, while ensuring the temperature remained within the range of 0 to 5°C. The reaction mixture was initially stirred at room temperature for 5–10 minutes, followed by heating to reflux. A solid product with a lemon-yellow color was obtained, filtered, and subjected to drying in oven at 40° C.²

3. Electronic Supplementary Information for DAP-AAQ (S_{3.1})

IUPAC: 2,2',2'',2''',2''''',2''''''',2''''''''',2'''''''''''-((15,35,55,75-tetraacetyl-2,4,6,8-tetrapropyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octayl)-octakis(oxy))octakis(N-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide)

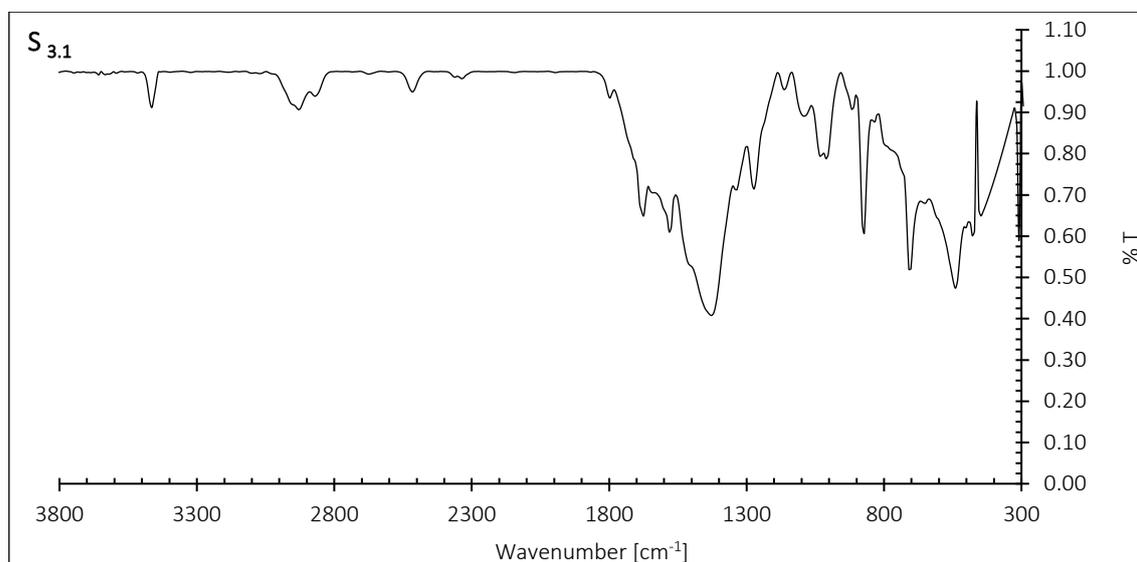


Fig S1: FT-IR Spectra of DAP-AAQ (S_{3.1})

FT-IR (KBr) ν : 3463cm⁻¹ (NH)_{stretching}, 2923cm⁻¹ (Alkane CH)_{stretching}, 1681cm⁻¹ (O=C-CH₃)_{stretching}, 1583cm⁻¹ (Amide C=O)_{stretching}, 1434cm⁻¹ (Aromatic C=C)_{stretching}, 1272cm⁻¹ (Alkyl Aryl Ether)_{stretching} [Fig S1]

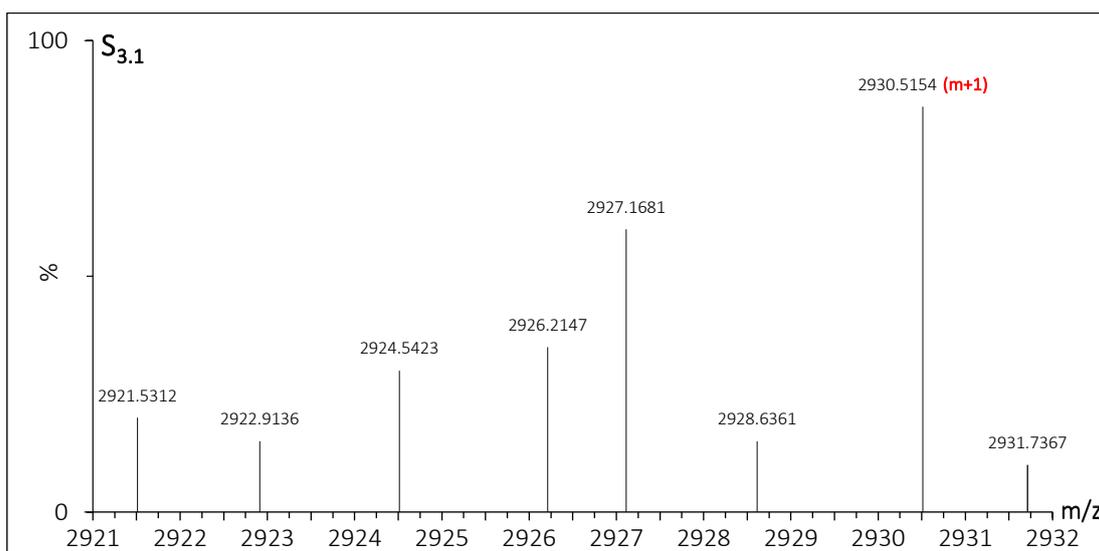


Fig S2: HR-MS Spectra of DAP-AAQ S_{3.1}

HR-MS: m/z for C₁₇₆H₁₂₈N₈O₃₆: **Calcd:** 2928.98, **found:** 2930.51 [Fig S2]

4. Electronic Supplementary Information for DAP-AAQ (S_{3.2})

IUPAC: 2,2',2'',2''',2''''',2''''''',2''''''''',2'''''''''''-((15,35,55,75-tetraacetyl-2,4,6,8-tetrabutyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶octayl)octakis(oxy))octakis(N-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide)

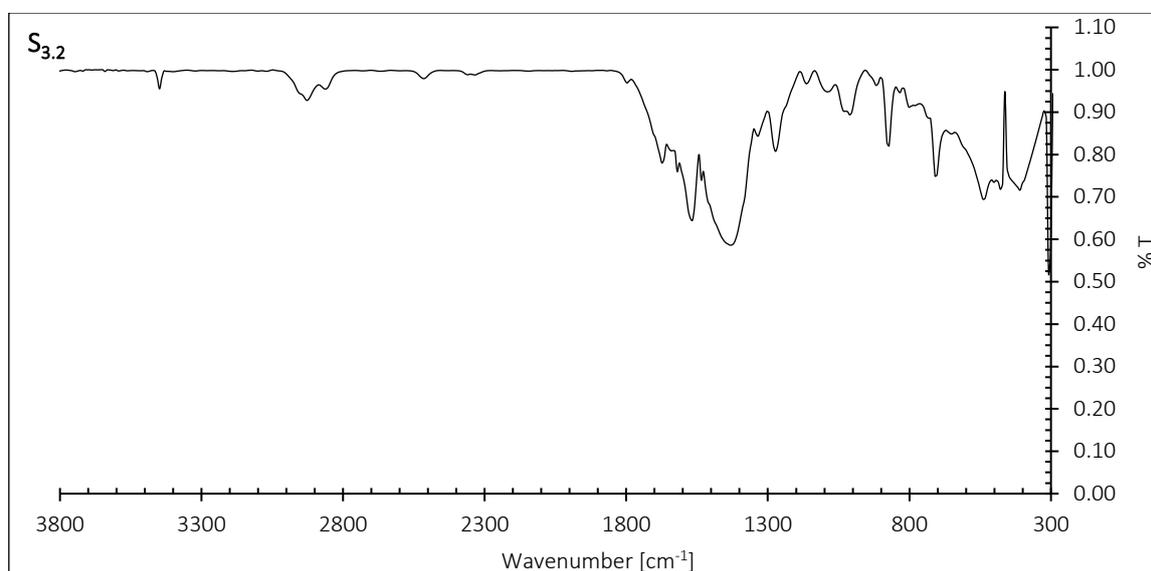


Fig S5: FT-IR Spectra of DAP-AAQ (S_{3.2})

FT-IR (KBr) ν : 3448 cm⁻¹ (NH)_{stretching}, 2924 cm⁻¹ (Alkane CH)_{stretching}, 1674 cm⁻¹ (O=C-CH₃)_{stretching}, 1566 cm⁻¹ (Amide C=O)_{stretching}, 1427 cm⁻¹ (Aromatic C=C)_{stretching}, 1273 cm⁻¹ (Alkyl Aryl Ether)_{stretching} [Fig S5]

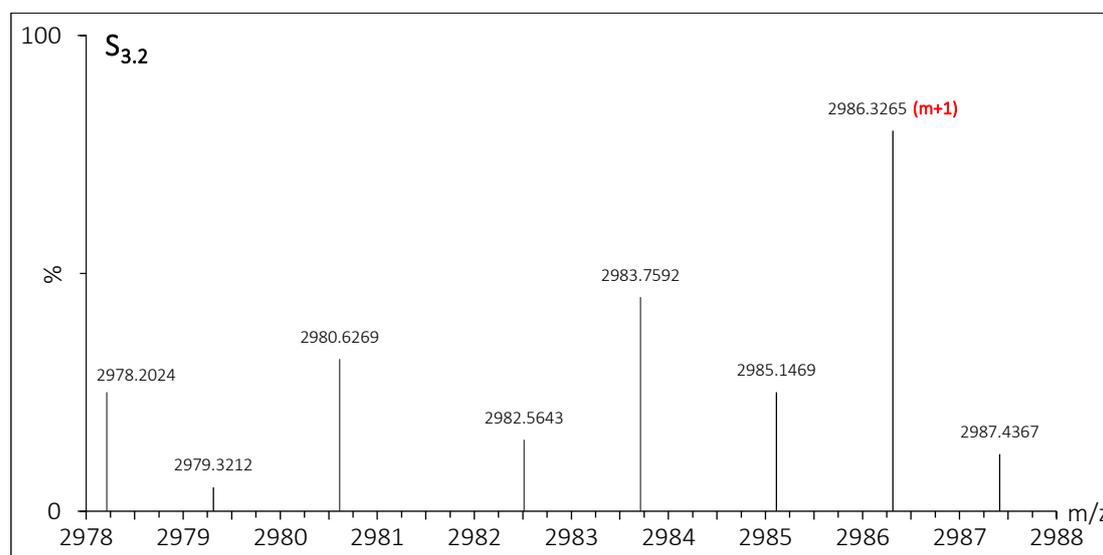


Fig S6: HR-MS Spectra of DAP-AAQ S_{3.2}

HR-MS: m/z for C₁₈₀H₁₂₆N₈O₃₆: Calcd: 2984.91, found: 2986.32 [Fig S6]

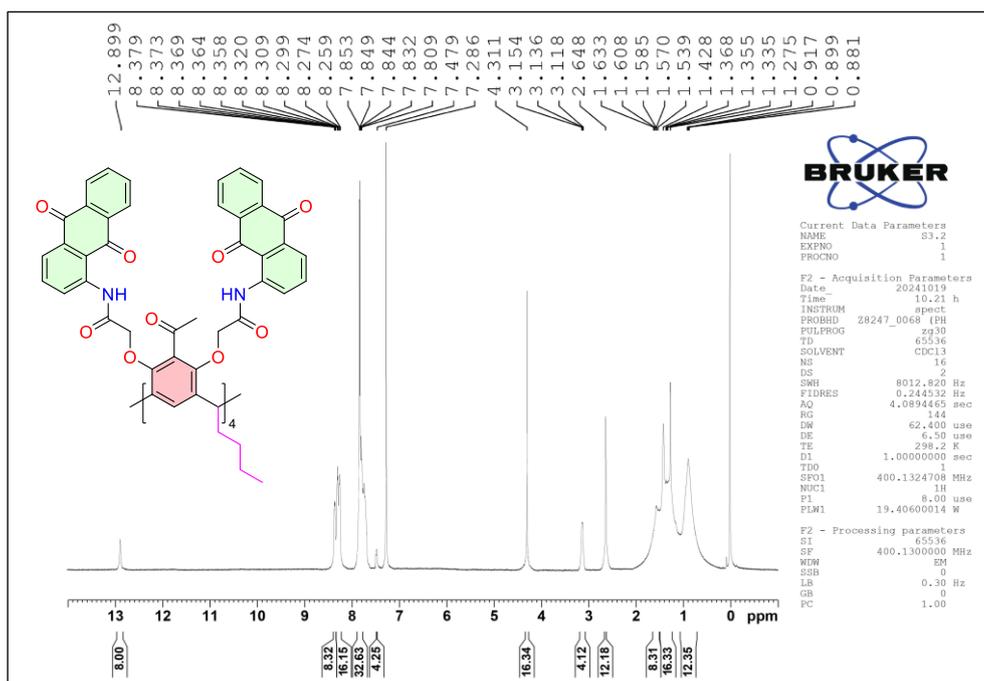


Fig S7: ¹H NMR Spectra of DAP-AAQ (S_{3.2})

¹H NMR (400 MHz, CDCl₃): 12.90 (8H, s, NH), 8.38-8.35 (8H, m, Anthraquinone CH), 8.32-8.25 (16H, m, Anthraquinone CH), 7.85-7.47 (32H, m, Anthraquinone CH), 7.48 (4H, s, Ar-CH), 4.31 (16H, s, O-CH₂), 3.15-3.12 (4H, t, J=7.2 Hz, -CH), 2.65 (12H, s, -CO-CH₃), 1.63-1.53 (8H, m, Aliphatic CH₂), 1.42-1.33 (16H, m, Aliphatic CH₂), 1.27-0.90 (12H, t, J=7.2 Hz, Aliphatic CH₃) [Fig S7]

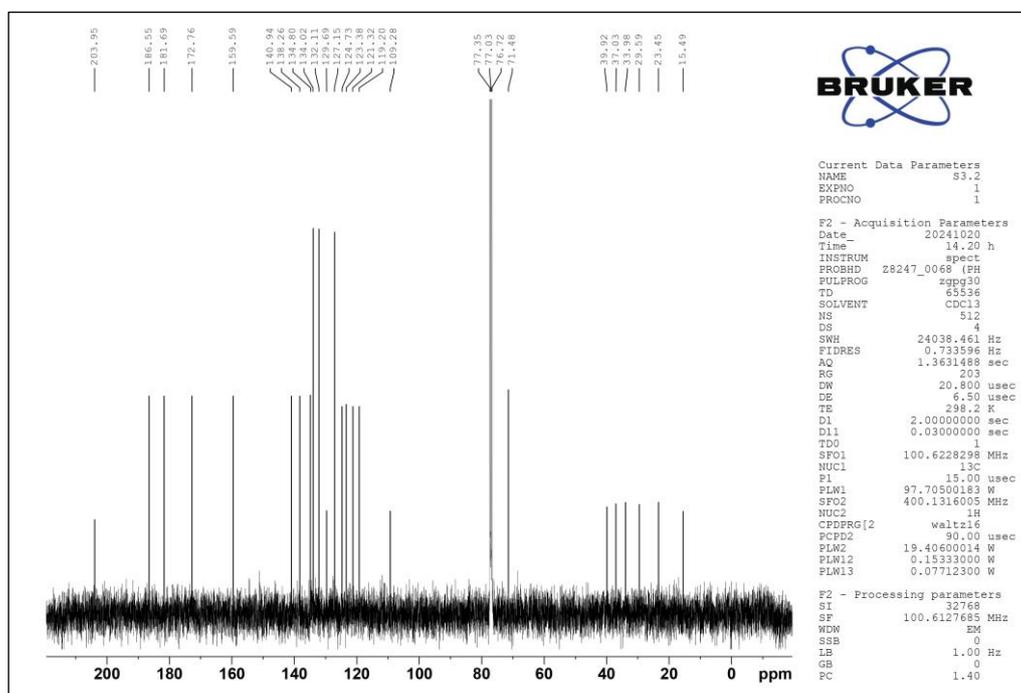


Fig S8: ¹³C NMR Spectra of DAP-AAQ (S_{3.2})

5. Electronic Supplementary Information for DAP-AAQ (S_{3.3})

IUPAC: 2,2',2'',2''',2''''',2''''''',2''''''''',2'''''''''''-((15,35,55,75-tetraacetyl-2,4,6,8-tetrahexyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octayl)octakis(oxy))octakis(N-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide)

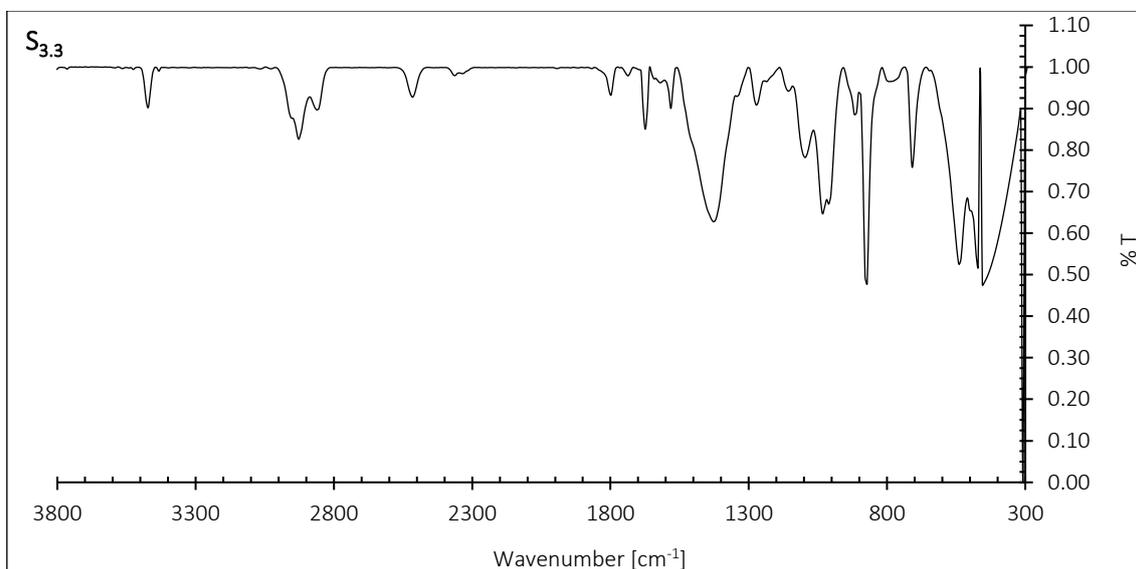


Fig S9: FT-IR Spectra of DAP-AAQ (S_{3.3})

FT-IR (KBr) ν : 3471 cm⁻¹ (NH)_{stretching}, 2926 cm⁻¹ (Alkane CH)_{stretching}, 1673 cm⁻¹ (O=C-CH₃)_{stretching}, 1581 cm⁻¹ (Amide C=O)_{stretching}, 1426 cm⁻¹ (Aromatic C=C)_{stretching}, 1272 cm⁻¹ (Alkyl Aryl Ether)_{stretching} [Fig S9]

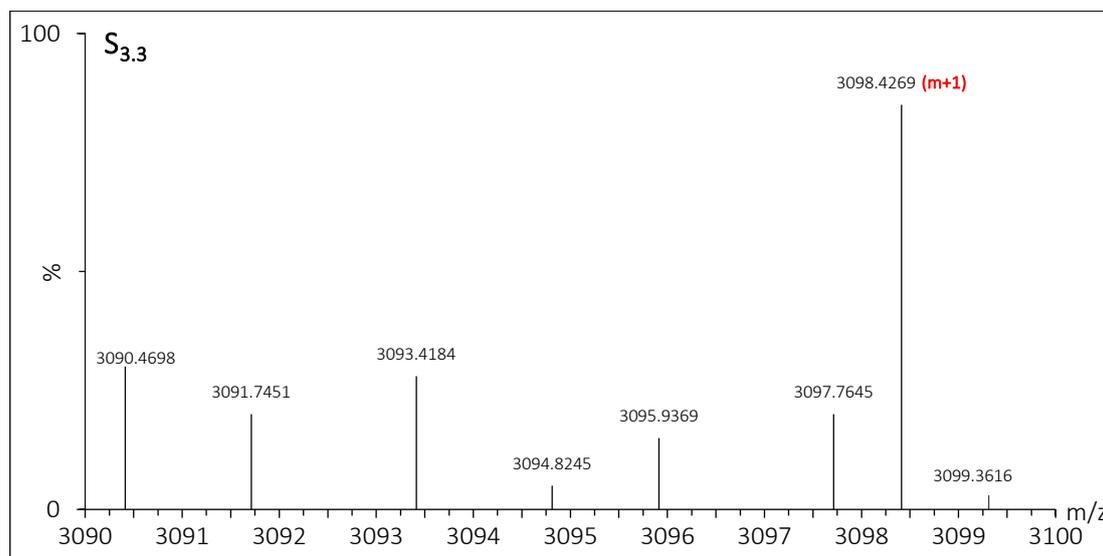


Fig S10: HR-MS Spectra of DAP-AAQ S_{3.3}

HR-MS: m/z for C₁₈₈H₁₅₂N₈O₃₆: Calcd: 3097.03, found: 3098.42 [Fig S10]

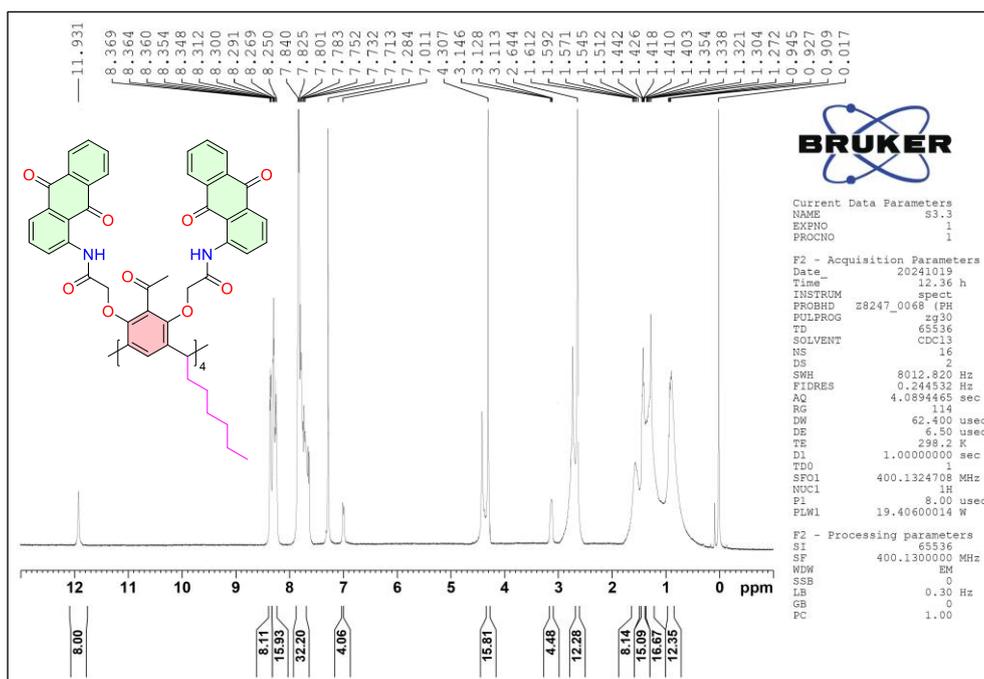


Fig S11: ^1H NMR Spectra of DAP-AAQ ($S_{3.3}$)

^1H NMR (400 MHz, CDCl_3): 11.93 (8H, s, NH), 8.37-8.35 (8H, m, Anthraquinone CH), 8.31-8.25 (16H, m, Anthraquinone CH), 7.84-7.71 (32H, m, Anthraquinone CH), 7.01 (4H, s, Ar-CH), 4.31 (16H, s, O- CH_2), 3.15-3.11 (4H, t, $J=7.2$ Hz, -CH), 2.65 (12H, s, -CO- CH_3), 1.61-1.51 (8H, Aliphatic CH_2), 1.44-1.40 (16H, Aliphatic CH_2), 1.35-1.27 (16H, Aliphatic CH_2), 0.94-0.91 (12H, t, $J=7.2$ Hz, Aliphatic CH_3) [Fig S11]

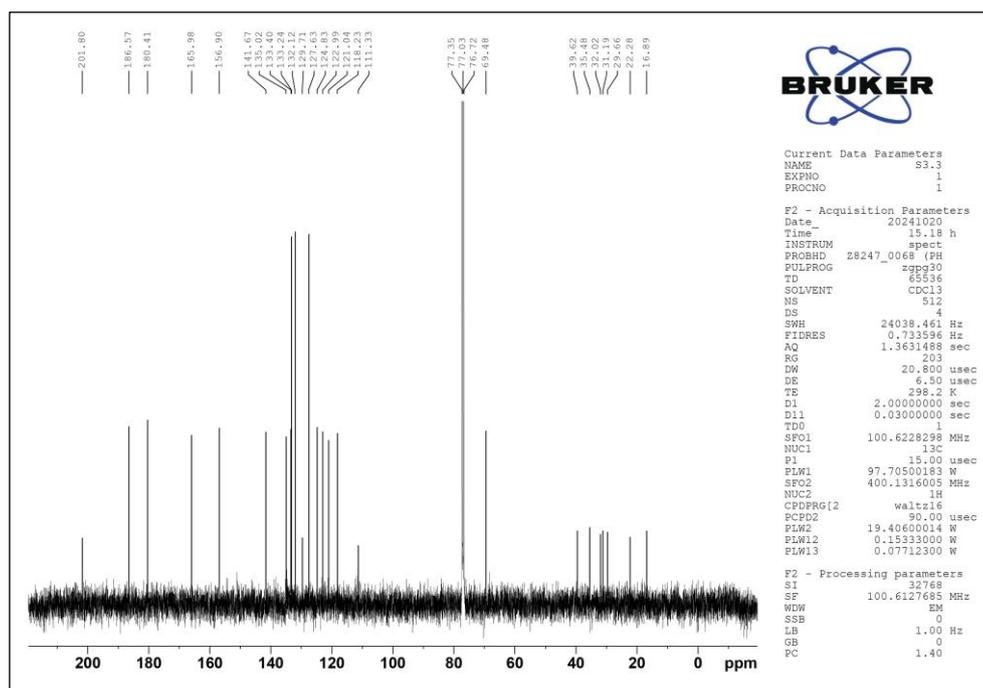


Fig S12: ^{13}C NMR Spectra of DAP-AAQ ($S_{3.3}$)

6. Electronic Supplementary Information for DAP-AAQ ($S_{3,4}$)

IUPAC: 2,2',2'',2''',2''''',2''''''',2''''''''',2'''''''''''-((15,35,55,75-tetraacetyl-2,4,6,8-tetraheptyl-1,3,5,7 (1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octayl)octakis(oxy))octakis(N-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide)

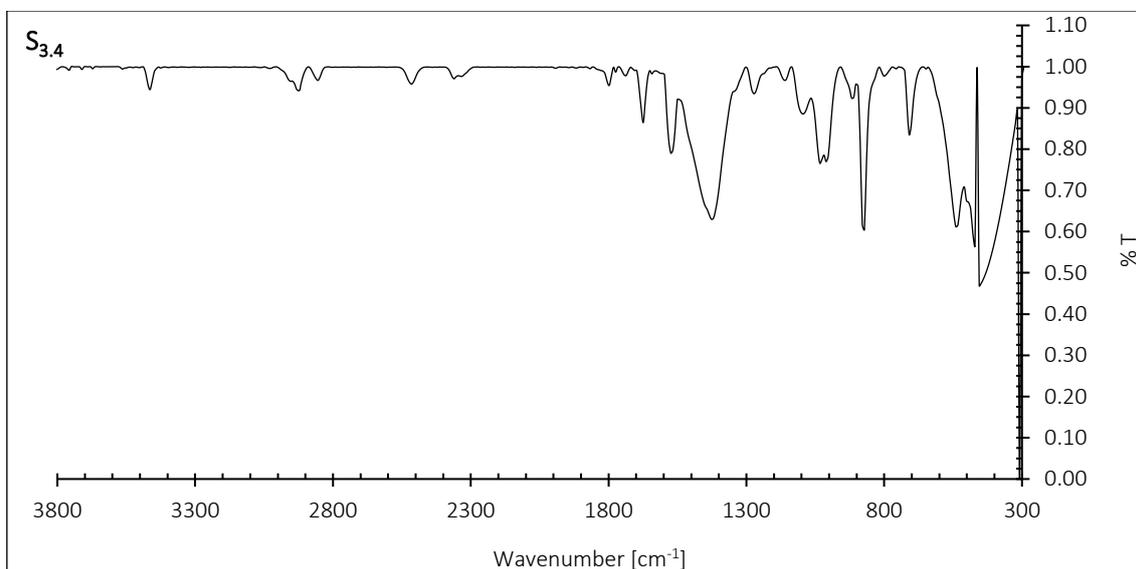


Fig S13: FT-IR Spectra of DAP-AAQ ($S_{3,4}$)

FT-IR (KBr) ν : 3463 cm^{-1} (NH)_{stretching}, 2921 cm^{-1} (Alkane CH)_{stretching}, 1679 cm^{-1} (O=C-CH₃)_{stretching}, 1573 cm^{-1} (Amide C=O)_{stretching}, 1419 cm^{-1} (Aromatic C=C)_{stretching}, 1271 cm^{-1} (Alkyl Aryl Ether)_{stretching} [Fig S13]

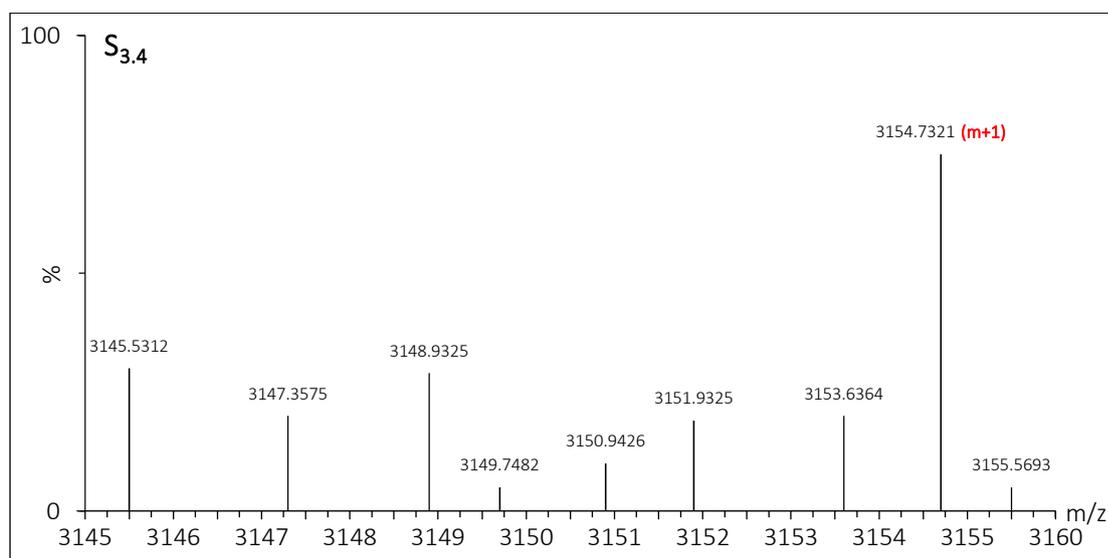


Fig S14: HR-MS Spectra of DAP-AAQ $S_{3,4}$

HR-MS: m/z for for $\text{C}_{192}\text{H}_{160}\text{N}_8\text{O}_{36}$: Calcd: 3153.09, found: 3154.73 [Fig S14]

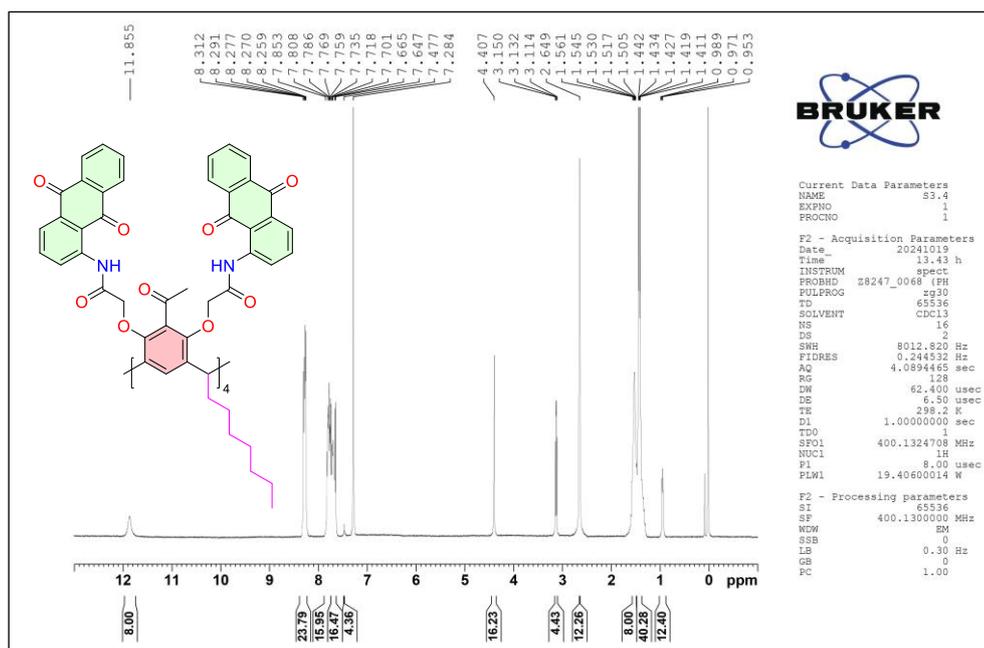


Fig S15: ^1H NMR Spectra of DAP-AAQ ($S_{3.4}$)

^1H NMR (400 MHz, CDCl_3): 11.86 (8H, s, NH), 8.31-8.26 (24H, m, Anthraquinone CH), 7.85-7.76 (16H, m, Anthraquinone CH), 7.74-7.65 (16H, m, Anthraquinone CH), 7.47 (4H, s, Ar-CH), 4.40 (16H, s, O- CH_2), 3.15-3.11 (4H, t, $J=7.2$ Hz, -CH), 2.65 (12H, s, -CO- CH_3), 1.56-1.50 (8H, Aliphatic CH_2), 1.44-1.41 (40H, Aliphatic CH_2), 0.99-0.95 (12H, t, $J=7.2$ Hz, Aliphatic CH_3) [Fig S15]

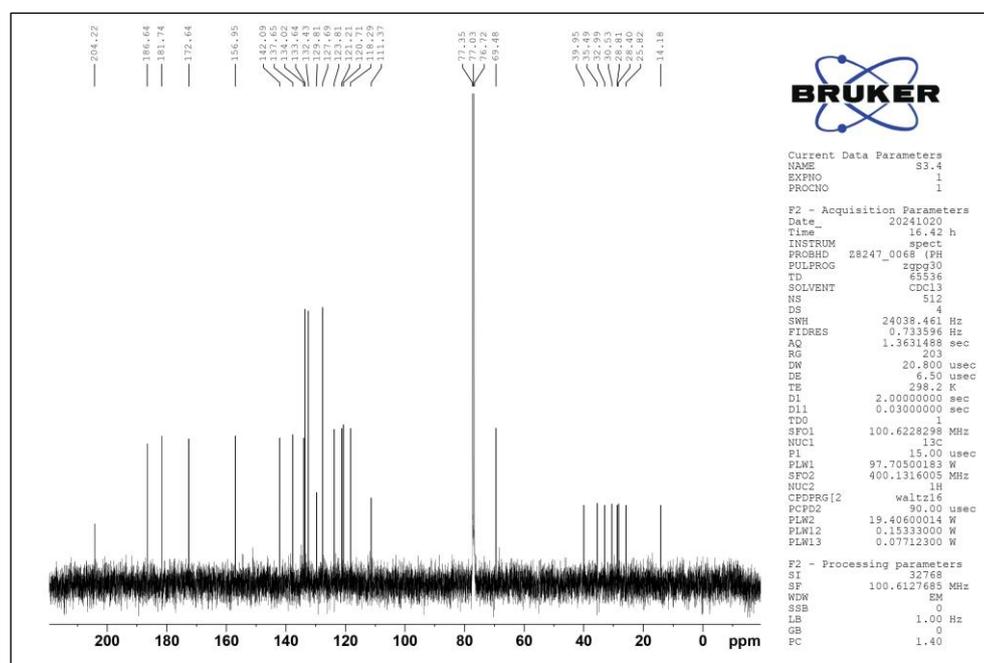


Fig S16: ^{13}C NMR Spectra of DAP-AAQ ($S_{3.4}$)

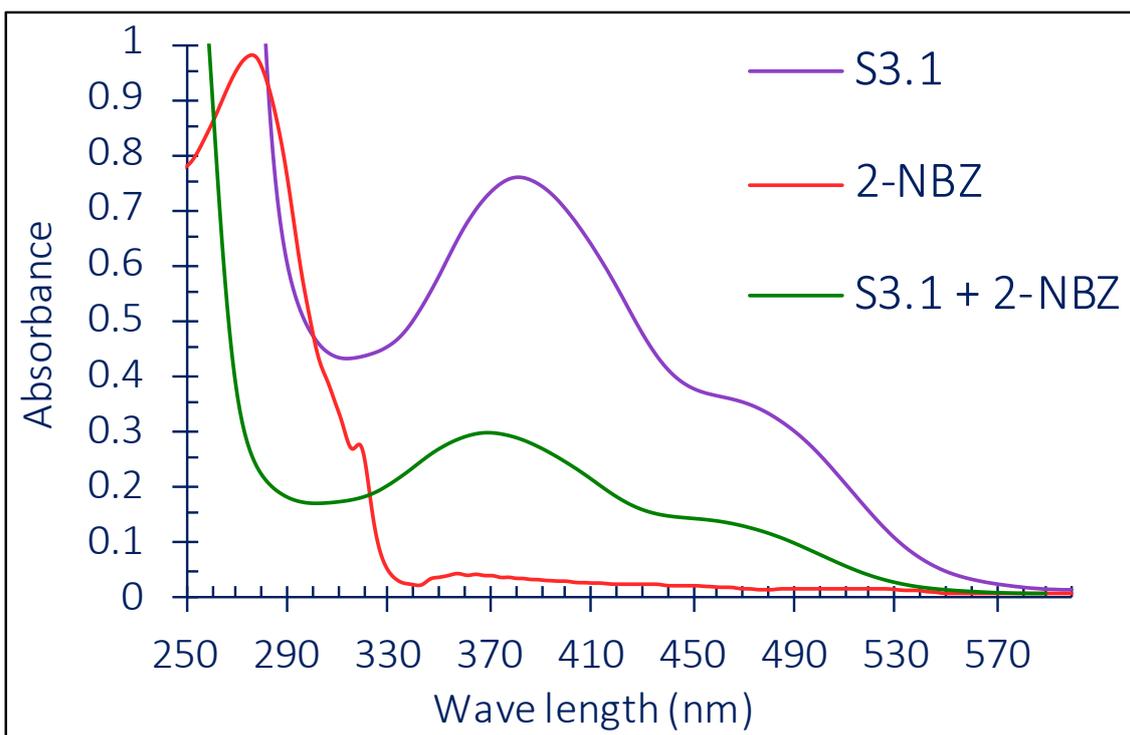


Fig S17: Absorbance spectral changes of DAP-AAQ ($S_{3.1}$), 2-nitrobenzaldehyde (2-NBZ) and $S_{3.1}+2\text{-NBZ}$

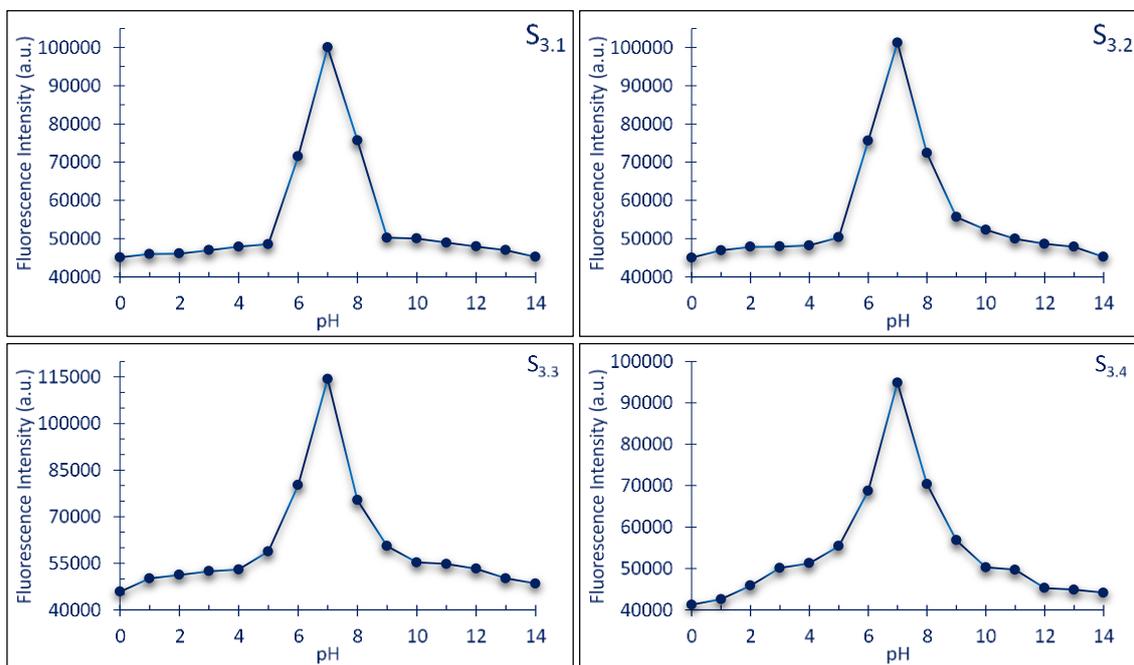


Fig S18: Fluorescence intensity of DAP-AAQ at different pH values in the presence of 2NBZ

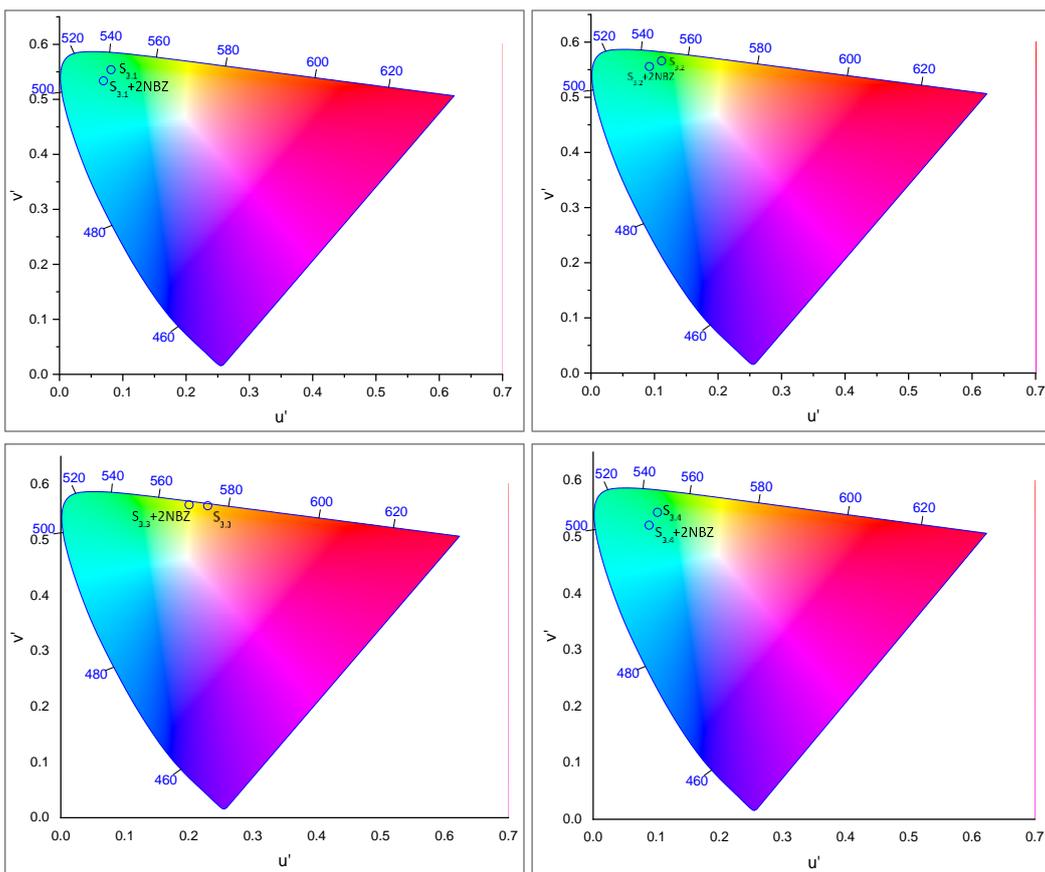


Fig S19: Colorchromaticity1976 (x,y) diagram of DAP-AAQ and DAP-AAQ + 2-NBZ

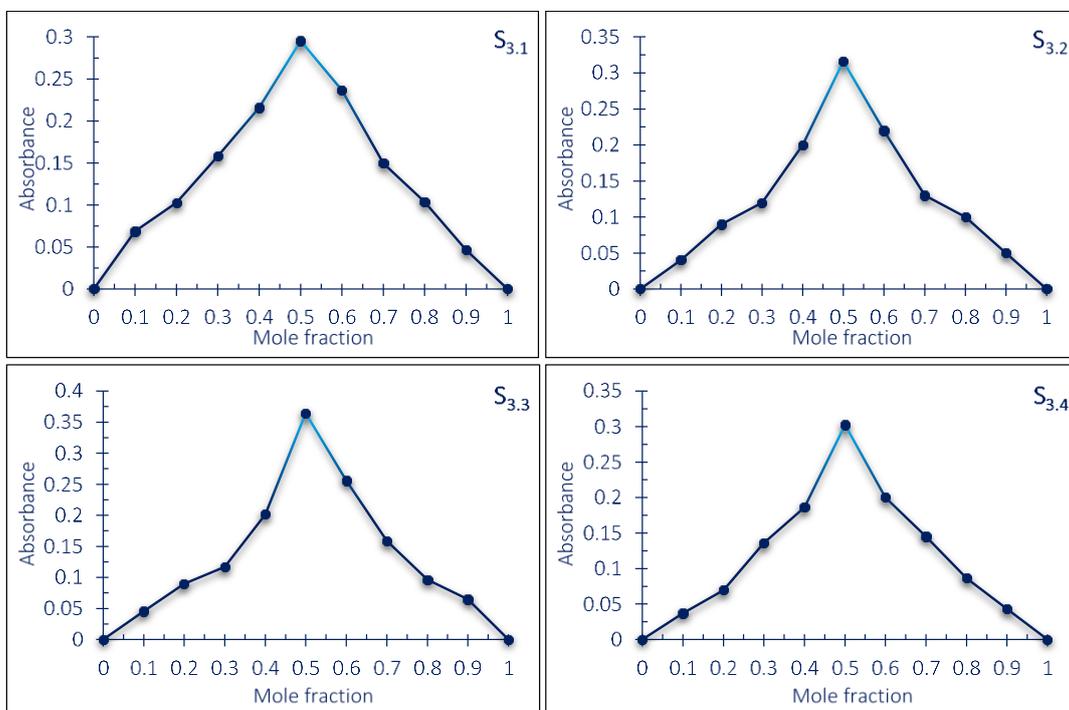


Fig S20: Job plot showing 1:1 stoichiometry of DAP-AAQ

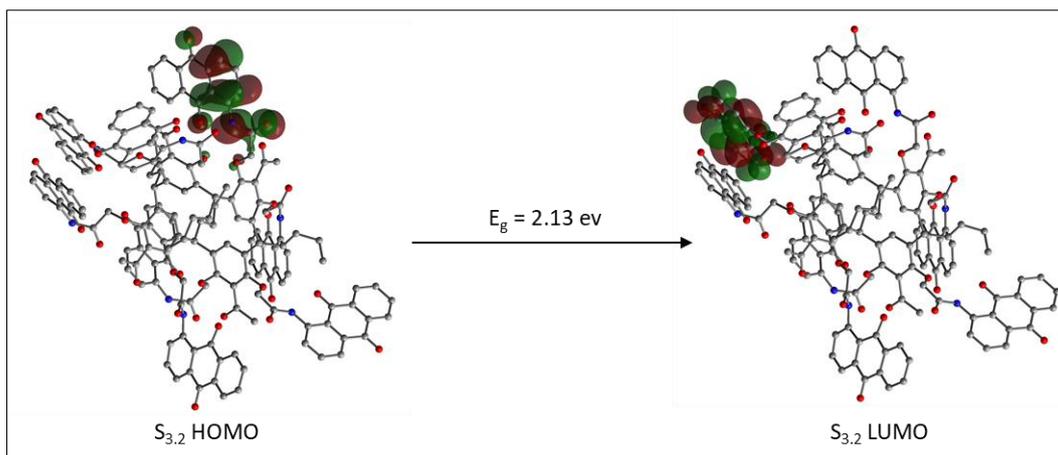


Fig S21: HOMO to LUMO transition in DAP-AAQ ($S_{3,2}$)

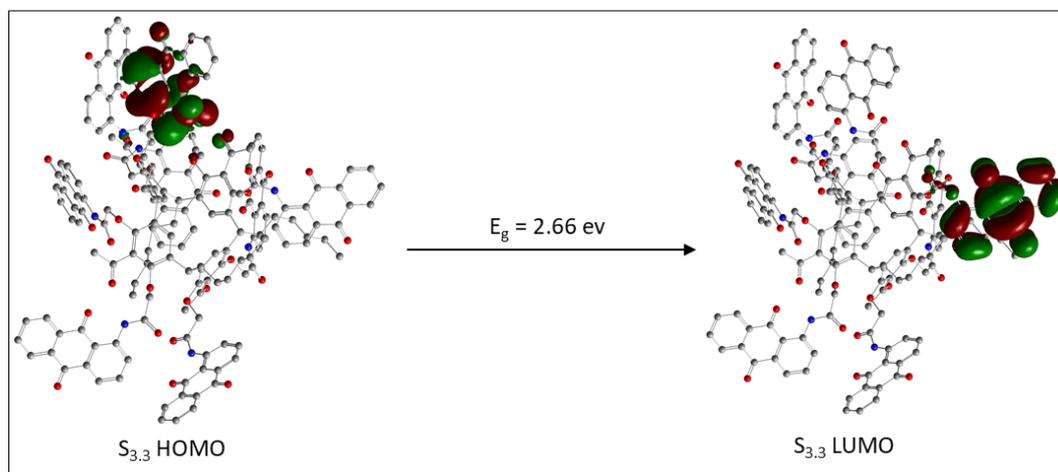


Fig S22: HOMO to LUMO transition in DAP-AAQ ($S_{3,3}$)

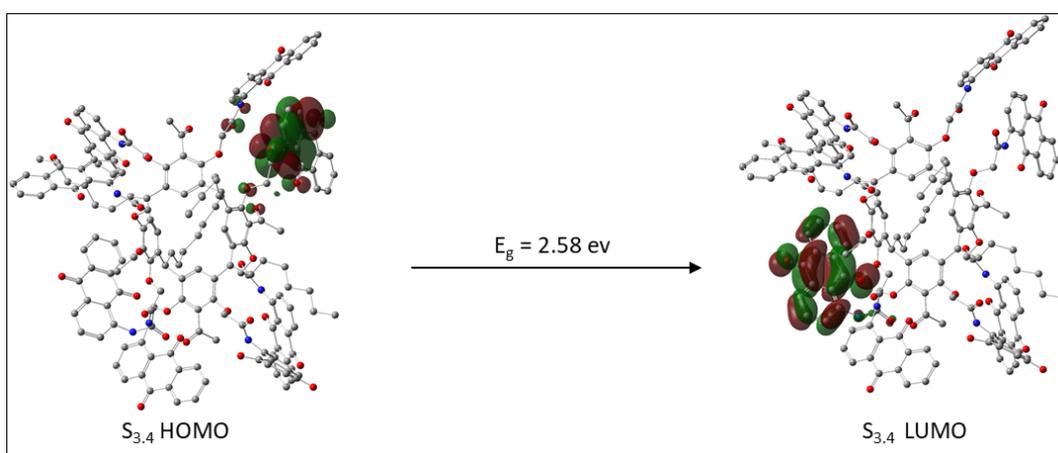


Fig S23: HOMO to LUMO transition in DAP-AAQ ($S_{3,4}$)

ESI Table 1:
Overview of calixarene-derived sensors for nitroaromatic compounds reported over the recent years

No.	Receptor	Analytes	Binding Constant	LOD	Ref
1	Thiacalix[4]arene bis-naphthalene sulfonate (TCDNS)	4-nitrotoluene, 2,3 dinitrotoluene	$2.37 \times 10^5 \text{ M}^{-1}$, $1.66 \times 10^4 \text{ M}^{-1}$	4.48 nM, 6.20 nM	3
2	Oxacalix[4]arene derivatives (FON3PPh)	4-nitrotoluene,	$1.15 \times 10^4 \text{ M}^{-1}$	2.40 μM	4
3	Oxacalix[4]arene derivatives (PON3PPh)	2,6-dinitrotoluene	$3.02 \times 10^4 \text{ M}^{-1}$,	0.10 μM	4
4	pyrene appended supramolecular assembly (PAOC)	4-nitrophenol (4NP), 2,4,6-trinitrophenol (TNP)	$0.74 \times 10^5 \text{ M}^{-1}$, $2.79 \times 10^5 \text{ M}^{-1}$	1.90 μM , 1.60 μM	5
5	Bisnaphthylated-azacalix[4]arene (BNAC)	Monocrotophos (MCP), N-methyl 4-nitroaniline (MNA)	$1.60 \times 10^6 \text{ M}^{-1}$, $1.07 \times 10^4 \text{ M}^{-1}$	5.50 μM , 0.50 μM	6
6	Oxacalix[4] arene-based ligand (DMANSOC)	2,4,6-Trinitrophenol	$2.45 \times 10^4 \text{ M}^{-1}$	4.64 μM	7
7	Napthalamide conjugated calix[4]arene	2,4,6-Trinitrophenol	-	29.00 nM	8
8	MOF [La(HTCPE)(H ₂ O)] ₂	4-nitroaniline (4-NA)		5.68 μM	9
9	MOF Zr-UiO-66-N ₂ H ₃	phosphate (PO ₄ ³⁻), 4-nitrobenzaldehyde (4-NB)	-	0.196 μM , 4.70 μM	10
10	Nitrogen-sulfur-codoped carbon nanoparticles (N,S-CNPs)	2,4,6-Trinitrophenol (TNP)	-	43.0 nM	11
11	2,6-Dihydroxyacetophenone[4]arene derivatives (DAP-AAQ: S _{3.1} , S _{3.2} , S _{3.3} , S _{3.4})	2-nitrobenzaldehyde	$2.00 \times 10^5 \text{ M}^{-1}$, $1.82 \times 10^5 \text{ M}^{-1}$, $1.67 \times 10^5 \text{ M}^{-1}$, $1.54 \times 10^5 \text{ M}^{-1}$	0.25 μM , 0.35 μM , 0.41 μM , 0.46 μM	This Work

REFERENCES

- 1 J Upadhyay and H Parekh, *Current Chemistry Letters*, 2019, 225-237.
- 2 R S Patel, R J Bhadoriya, K M Modi, M A Vora, M N Patel and H M Parekh, *Talanta*, 2025, **285**, 127322.
- 3 K Modi, U Panchal, C Patel, K Bhatt, S Dey, D Mishra and V K Jain, *New Journal of Chemistry*, 2018, **42**, 2682-2691.
- 4 M Panchal, A Kongor, M Athar, K Modi, C Patel, S Dey, M Vora, K Bhadresha, R Rawal, P C Jha and V K Jain, *Journal of Molecular Liquids*, 2020, **306**, 112809.
- 5 V Desai, M Vora, K Modi, B Koley Seth, F Panjwani, A Verma, N Patel, C Patel and V K Jain, *ChemistrySelect*, DOI:10.1002/slct.202302029.
- 6 S Dey, K Modi, U Panchal, M Panchal and V K Jain, *Journal of Molecular Liquids*, 2021, **337**, 116337.
- 7 V Desai, K Modi, F Panjwani, B K Seth, M Vora, J Parikh and V K Jain, *Journal of Fluorescence*, 2024, **34**, 1219-1228.
- 8 A Narula, M A Hussain, A Upadhyay and C P Rao, *ACS Omega*, 2020, **5**, 25747-25756.
- 9 N Song, W Li, W Luo, Z Zhai, S Wang, R Huai, D Zhang, Z Zhou and L Yang, *Journal of Solid State Chemistry*, 2022, **316**, 123568.
- 10 A Das, S Das, V Trivedi and S Biswas, *Dalton Transactions*, 2019, **48**, 1332-1343.
- 11 W Lai, J Guo, N Zheng, Y Nie, S Ye and D Tang, *Analytical and Bioanalytical Chemistry*, 2020, **412**, 3083-3090.