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Research Paper

Design and Spectroscopic Evaluation of Quinoline–Carbazole Hybrids for Metal-Ion Detection in Industrial Wastewater

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Abstract
Quinoline–carbazole hybrids combine a chemically adaptable coordination site with an aromatic framework capable of reporting changes in its electronic environment. Their application to industrial wastewater requires the optical response to remain interpretable in the presence of competing ions, dissolved organic matter and variable acidity. This paper develops a molecular design and analytical evaluation framework from literature published. Four neutral, carbon-linked hybrids are considered to separate the effects of an 8-hydroxyquinoline binding site and an ether-containing carbazole substituent. Published measurements from related heterocyclic probes provide quantitative benchmarks, while calculations examine the consequences of spectral displacement, dilution and optical attenuation. A carbazole–pyrimidine precedent exhibits a copper-induced emission displacement from 505 to 663 nm, although its measurements were obtained in a mixture containing 70% tetrahydrofuran. Reported copper detection limits from two distinct carbazole systems correspond to approximately 1.33 and 360 μg L^{-1}, illustrating the range of analytical performance that different architectures and conditions can produce. The proposed evaluation integrates structural verification, absorption and fluorescence measurements, binding analysis and comparison with elemental spectrometry. The analysis identifies accessible quinoline coordination, controlled aqueous speciation and matrix-specific calibration as the main requirements for advancing these hybrids towards wastewater monitoring. The numerical results are attributed literature measurements and explicit calculations; experimental evaluation of the proposed series remains prospective.

Keywords: *Quinoline–carbazole hybrids; fluorescent chemosensors; metal-ion detection; industrial wastewater; coordination chemistry; analytical validation.*

I. Introduction

Metal-ion monitoring in industrial wastewater is complicated by the chemical and optical properties of the surrounding solution. Dissolved organic compounds can bind metals, absorb excitation light and contribute their own fluorescence. These effects change during treatment. In a full-scale coking-wastewater study, Xu et al. identified distinct protein-like and humic-like fluorescent components and related spectral indices to water-quality parameters [1]. A molecular probe introduced into such a matrix encounters an existing optical signal as well as an analyte.

Elemental spectrometry provides a reference against which a proposed optical measurement can be assessed. United States Environmental Protection Agency Method 200.7 describes the determination of metals in water and wastes by inductively coupled plasma atomic emission spectrometry, including different preparation requirements for dissolved and total-recoverable fractions [2]. A fluorescent ligand usually responds to metal available for association or reaction under the assay conditions. Establishing the relationship between that response and the selected elemental fraction is therefore central to its environmental interpretation.

Quinoline and carbazole offer complementary functions within a molecular sensor. The pyridine-like quinoline nitrogen can participate in coordination, whereas the carbazole framework provides an electron-rich aromatic component. Li and Gao demonstrated direct carbon-linked quinoline–carbazole synthesis through Friedländer condensation [3]. Feng et al. subsequently showed that the arrangement of pyridine acceptors and carbazole donors affects charge transfer and cation recognition [4]. These precedents support a design in which a defined coordination event is electronically coupled to the chromophore.

Several earlier studies establish the breadth of the optical response. Yang et al. reported a carbazole Schiff base responsive to Fe(III) and Cu(II) [5], while Kaur et al. obtained different long-wavelength responses to Hg(II) and Cu(II) from a carbazole–pyrimidine conjugate [6]. Quinoline receptors also display structure-dependent discrimination: Kim et al. described a zinc-responsive receptor that distinguished Zn(II) from Cd(II) [7], and Zhang et al. developed a reactive quinoline probe for Hg(II) [8]. Coordination, chemical transformation and changes in excited-state relaxation consequently need to be examined as distinct origins of a spectral response.

Aqueous compatibility is equally dependent on molecular construction. Tao et al. incorporated quinoline into an amphiphilic probe responsive to trivalent cations [9], and Bell et al. investigated substituted 8-hydroxyquinoline sensors for mercury recognition [10]. These findings motivate the combination of a chelating quinoline unit with a substituent intended to improve solution handling. The present paper develops that connection through a matched hybrid series and evaluates the analytical implications of earlier measurements. Its objective is a chemically testable route from molecular design to wastewater analysis, grounded in evidence available before the end of 2015.

II. Molecular design and synthetic rationale

The proposed series retains a direct bond between carbazole C3 and quinoline C2. Quinoline N1 remains unquaternised, preserving its lone pair for coordination. This connectivity differs from an alkyl-linked quinolinium salt, in which quaternisation consumes the nitrogen lone pair and introduces permanent charge. Carbazole N9 is substituted in all four members; its pyrrolic lone pair is part of the aromatic system and is not treated as the principal metal-binding site.

Table 1 defines two controlled structural changes. An 8-hydroxyl group introduces a potential N,O-chelating site adjacent to quinoline nitrogen, while an ether-containing N9 substituent changes side-chain polarity. QCH1 corresponds to the neutral 9-ethyl-3-(quinolin-2-yl)carbazole structure reported by Li and Gao [3] and provides a reference structure. QCH2–QCH4 are design candidates whose properties would be determined experimentally. The matrix permits the influence of hydroxyl substitution to be examined independently of the N9 side chain.

Table 1. Matched quinoline–carbazole design series.

Code	Carbazole N9 group	Quinoline C8 group	Design role
QCH1	Ethyl	H	Published reference structure [3]
QCH2	Ethyl	OH	Proposed N,O-binding analogue
QCH3	2-(2-Methoxyethoxy)ethyl	H	Proposed polar-side-chain analogue
QCH4	2-(2-Methoxyethoxy)ethyl	OH	Proposed combined modification

The 8-hydroxyquinoline unit offers a chemically established route to metal association. Li, Gao and Fang incorporated this group into a silica-supported chelating material and reported uptake of Cu(II) and Ni(II) [11]. That work concerns adsorption rather than fluorescence, but it supports the coordination role of the N,O donor arrangement. In the proposed soluble hybrids, the same donor arrangement may influence both binding and excited-state behaviour. The magnitude and selectivity of the optical response will depend on the complete structure, its protonation state and the composition of the medium.

The synthetic starting point is an N9-substituted carbazole bearing an acetyl group at C3. Condensation with an appropriate ortho-amino aromatic aldehyde would construct the quinoline ring. The earlier neutral series was obtained using sodium ethoxide in ethanol, with isolated yields of 52–72% across mono- and bis-substituted products [3]. An appropriately hydroxyl-substituted precursor, with protection where required, would extend this route to the 8-hydroxyquinoline members. The compatibility of the ether side chain and the hydroxyl group with acetylation, cyclisation and purification would be established during route optimisation.

Structural verification would combine ^{1}H and ^{13}C NMR with COSY, HSQC and HMBC experiments. Correlations around the quinoline and carbazole junction would establish the carbon-linked architecture, while side-chain integration would distinguish the ethyl and ether-containing derivatives. High-resolution mass spectrometry would test elemental composition, and analytical chromatography would assess residual precursors and closely related impurities. The appearance or disappearance of a hydroxyl resonance alone would be insufficient for assignment because exchange depends on solvent and water content. Purity and compound content would be established before preparing calibration solutions.

III. Spectroscopic and analytical framework

3.1 Solution conditions and optical measurements

The evaluation would begin by determining solubility, spectral stability and concentration-dependent association in water–organic solvent mixtures. The organic fraction would be held constant within each comparison and progressively reduced where the compounds remain molecularly dispersed. An initial pH interval of 4–8 would provide a practical screening window, with protonation and hydrolysis controls interpreted separately. A buffer would be selected for each working interval after testing its influence on metal response. The buffer-design principles introduced by Good et al. provide a methodological starting point [12]; suitability for a particular metal–ligand system would still require direct comparison.

Absorption spectra would establish the concentration interval over which absorbance is proportional to concentration and would identify any baseline elevation associated with scattering. Emission and excitation spectra would then be recorded with instrument-response correction and fixed acquisition settings. Quantum yields would be determined against a suitable reference or by an integrating-sphere method, using the calibration principles described by Brouwer [13] and Würth et al. [14]. Independent solution preparations would distinguish preparation variability from repeated scans of the same sample.

Two descriptors are used for the published-data analysis:

$$B_{max} = \varepsilon_{max}\,\Phi_F \quad (1)$$

$$\Delta\tilde{\nu} = 10^7(1/\lambda_{abs} - 1/\lambda_{em}) \quad (2)$$

Here B_{max} is peak molecular brightness in M^{-1} cm^{-1}, ε_{max} is the molar absorption coefficient, Φ_F is the dimensionless fluorescence quantum yield and wavelengths are expressed in nm. Equation (2) gives the wavenumber Stokes shift in cm^{-1}. These quantities describe different properties: a long-wavelength emission band may accompany a smaller wavenumber separation, while a lower quantum yield may be offset by stronger absorption. At a fixed instrument excitation wavelength, ε at that wavelength would replace ε_{max}.

Wastewater measurements require particular attention to inner-filter effects. Kubista et al. demonstrated an experimental approach to their correction [15], and Fonin et al. showed how absorbance, reabsorption and instrument geometry affect measured fluorescence [16]. Absorption measurements and dilution checks would therefore accompany every matrix study. Excitation spectra, fluorescence lifetimes and the persistence of the response after correction would help distinguish a change in molecular emission from attenuation of light by the sample.

3.2 Metal response and binding analysis

Cu(II) would be the principal analytical target, with Zn(II), Ni(II), Co(II), Fe(III), Cd(II), Pb(II), Hg(II), Al(III), Cr(III), Ca(II) and Mg(II) included in a broader response screen. Individual-ion measurements would be followed by target-plus-interferent mixtures. The order of addition, equilibration time and dissolved appearance would be recorded because competition, slow exchange and precipitation can produce different outcomes. Fe(III) and Cr(III) responses would be interpreted within their actual solution conditions rather than compared solely at the same nominal concentration.

A coordination hypothesis would be examined through absorption, emission and mass-spectrometric changes, supplemented by NMR where the metal permits useful observation. Paramagnetic Cu(II) can broaden NMR signals; diamagnetic analogues may assist assignment but do not establish an identical geometry. Reversibility after addition of a stronger ligand and repeated response cycles would help distinguish equilibrium association from irreversible chemical transformation. These observations are especially relevant because reactive mercury probes and coordinating copper probes can exhibit superficially similar red-shifted signals [6], [8].

Binding constants would be estimated by fitting mass-balance models directly to titration data. Thordarson discusses the influence of model choice, concentration and fitting method on such estimates [17]. Competing 1:1 and higher-stoichiometry models would be assessed against residuals and independent structural evidence. Continuous-variation measurements can provide complementary information, as examined by Renny et al. [18], but a single maximum would not carry the complete assignment. Association constants obtained in different solvent and buffer conditions would be treated as conditional quantities.

3.3 Calibration and industrial wastewater validation

For a monotonic response, the analytical signal would be a corrected intensity or a ratio of two resolved emission bands. A ratio is useful when it reduces sensitivity to probe amount or excitation drift, although unequal attenuation at the two wavelengths can still introduce matrix dependence. Calibration would cover the experimentally established response interval, with independently prepared standards and replicate blanks. Currie's treatment of detection and quantification provides the statistical basis for distinguishing a detectable signal from a reliably quantified concentration [19].

$$LOD \approx 3s_{blank}/|m| \quad \text{and} \quad LOQ \approx 10s_{blank}/|m| \quad (3)$$

Equation (3) gives conventional preliminary estimates for a locally linear calibration with slope m and blank standard deviation s_{blank}. Performance near those estimates would be checked using low-concentration samples. Calibration-model adequacy, residual behaviour and uncertainty would be evaluated according to the framework of Danzer and Currie. A high coefficient of determination alone would not resolve curvature, concentration-dependent variance or a biased intercept.

The proposed application would compare untreated and treated effluents from metal-processing operations, with each collection event retained as an independent sample. Separate aliquots would support optical testing and elemental analysis. A filtered aliquot would define the operationally dissolved fraction, while an appropriately prepared unfiltered aliquot would support total-recoverable determination under Method 200.7 [2]. Acid-preserved elemental-analysis material would be distinguished from the aliquot used to investigate the original optical response, since acidification and subsequent neutralisation can change metal speciation.

Matrix validation would include reagent blanks, unspiked samples, additions at three concentration levels and an independent check standard. Standard additions and aqueous calibration would be compared to identify matrix-dependent sensitivity. Recovery would be calculated as $100(C_{spiked} - C_{unspiked})/C_{added}$, with every concentration referred to the same original-sample basis. Recovery of 90–110% and relative standard deviation below 5% above the quantification limit are proposed initial performance targets. Their suitability would be assessed against concentration, sample variability and the intended monitoring decision.

Agreement with elemental spectrometry would be evaluated through concentration differences and uncertainty, rather than correlation alone. Strong dissolved ligands may leave part of the metal inaccessible to the probe even when it remains measurable by ICP-AES. Where this occurs, the optical result would describe the assay-accessible fraction. Establishing this relationship is necessary before using a fluorescence response to follow treatment performance or identify changes in an effluent stream.

IV. Quantitative literature analysis

4.1 Spectral displacement and molecular brightness

The carbazole–pyrimidine study of Kaur et al. supplies a useful internally consistent photophysical comparison [6]. Table 2 brings together the reported long-wavelength absorption maxima, emission maxima, absorption coefficients and quantum yields. The Hg-treated state is identified as a reaction product because the study attributes its response to alkyne hydration; the Cu-treated state is discussed as a coordination response. Both were examined in THF–HEPES buffer at a 7:3 volume ratio and pH 7.4.

Table 2. Reported photophysical measurements and calculated brightness [6].

Chemical state	λ_{abs} (nm)	λ_{em} (nm)	ε_{max} (M^{-1} cm^{-1})	Φ_F	B_{max} (M^{-1} cm^{-1})
Free probe	403	505	23,100	0.62	14,322
Hg(II)-treated reaction product	552	657	32,800	0.59	19,352
Cu(II)-treated complex	582	663	34,700	0.54	18,738

The calculated brightness values increase from 14322 M^{-1} cm^{-1} for the free probe to 19352 and 18738 M^{-1} cm^{-1} for the Hg- and Cu-treated states, respectively. These correspond to increases of approximately 35.1% and 30.8%, despite lower quantum yields. The absorption change therefore contributes substantially to the brightness descriptor. Meanwhile, the calculated Stokes shift decreases from approximately 5012 to 2895 and 2099 cm^{-1}. Figure 1 places the spectral maxima on a common wavelength scale without reconstructing unreported spectral line shapes.

For the quinoline–carbazole design, the useful lesson is that spectral displacement and intensity should be interpreted together. Coordination may move a transition into a region with less wastewater background even when the total fluorescence yield does not increase. Conversely, a favourable peak-brightness value may provide little benefit if the available excitation wavelength overlaps weakly with the new absorption band. Recording complete excitation and emission profiles would resolve that distinction.

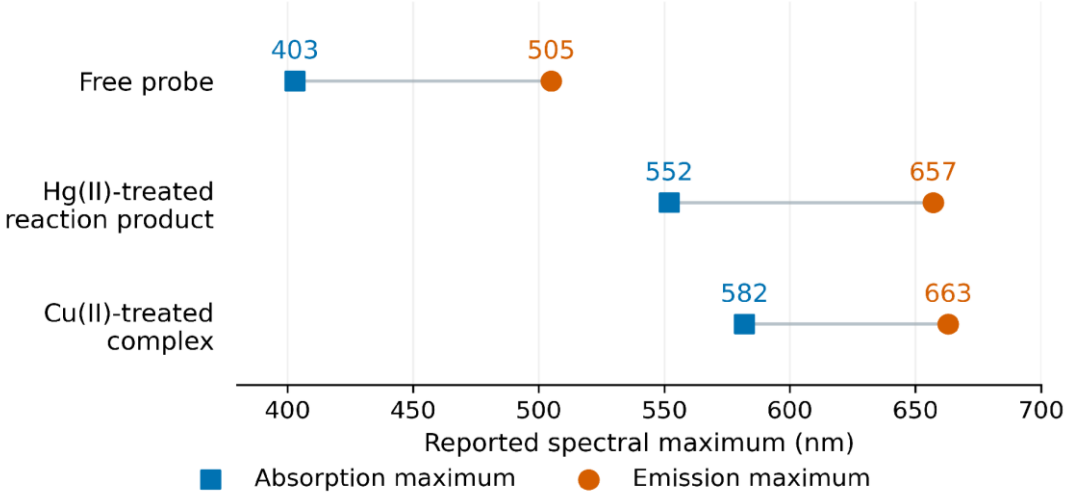


Figure 1. Published absorption and emission maxima for the free carbazole–pyrimidine probe and its Hg(II)- and Cu(II)-treated states [6]. Markers show reported peak positions; the connecting segments are guides and do not represent spectral line shapes.

The solvent composition also limits direct transfer of the benchmark to an aqueous application. A solution containing 70% THF differs substantially from an industrial effluent in dielectric environment, ligand competition and potential aggregation. The ether-containing QCH derivatives address one aspect of this problem through side-chain design. Their usefulness would depend on whether a lower organic-solvent fraction can be achieved while preserving the relationship between metal concentration and signal.

4.2 Detection limits on a common concentration basis

Table 3 places selected reported detection limits on both molar and mass-concentration scales. Yang et al. reported 4.23 µM for Fe(III) and 5.67 µM for Cu(II) using a carbazole Schiff base [5]. The copper detection limit reported for the carbazole–pyrimidine probe was 0.021 µM [6]. Conversion uses standard molar masses of 55.845 g mol⁻¹ for iron and 63.546 g mol⁻¹ for copper.

Probe system	Ion	Reported LOD (µM)	Calculated LOD (µg L⁻¹)	Ref.
Carbazole Schiff base	Fe(III)	4.23	236	[5]
Carbazole Schiff base	Cu(II)	5.67	360	[5]
Carbazole–pyrimidine	Cu(II)	0.021	1.33	[6]

Table 3. Published detection limits and corresponding mass concentrations.

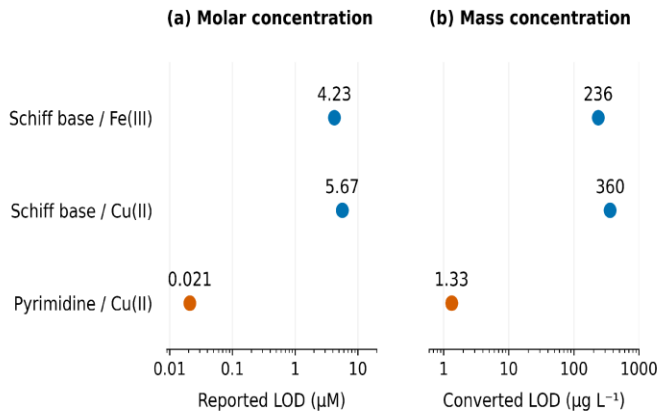


Figure 2. Detection limits for the carbazole Schiff base [5] and carbazole–pyrimidine probe [6], expressed as (a) reported molar concentration and (b) calculated mass concentration. Both horizontal axes are logarithmic.

The two copper values differ by a factor of 270. This numerical contrast reflects the combined influence of molecular architecture, solvent conditions, response function and detection-limit estimation. It is not an isolated measure of the benefit of replacing a Schiff base with a pyrimidine group. The datasets nevertheless establish a useful span for planning initial calibration concentrations and deciding whether dilution alone is compatible with the intended sample range.

Selectivity requires a separate assessment. A response to both Fe(III) and Cu(II) can be analytically useful when the ions occur separately or can be resolved by independent signals, but it creates ambiguity in a mixed effluent. Similarly, a red-shifted band is not intrinsically specific to a single element. The proposed series would therefore be judged by its performance in competitive mixtures and reference-characterised samples, alongside its response in individual-ion solutions.

4.3 Dilution and optical transmission

Dilution can reduce optical background, but it raises the detection limit referred to the original sample. To show the relationship without assuming a measured wastewater composition, Table 4 uses an explicitly calculated scenario with initial absorbance $A_0 = 1.00$, Beer–Lambert behaviour and no analyte loss. At dilution factor D, absorbance is A_0/D and transmitted incident light is $100 \times 10^{-A_0/D}$ percent. The original-sample detection limit is D times the final-assay detection limit.

Table 4. Calculated effect of dilution on transmission and original-sample Cu detection limits.

D	Assay absorbance	Transmission (%)	Pyrimidine Cu LOD (µg L^{-1})	Schiff-base Cu LOD (µg L^{-1})
1	1.00	10.0	1.33	360
2	0.50	31.6	2.67	721
5	0.20	63.1	6.67	1802
10	0.10	79.4	13.3	3603
20	0.05	89.1	26.7	7206

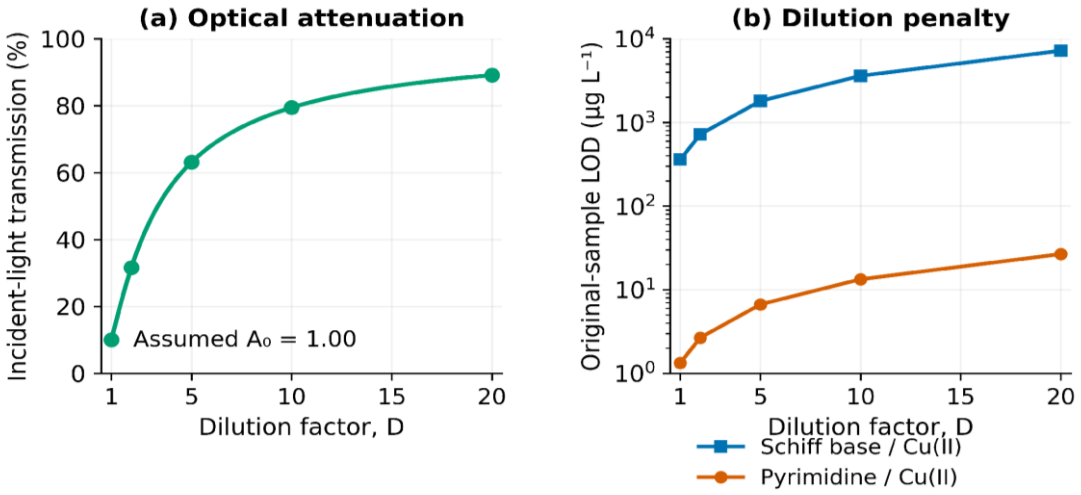


Figure 3. Calculated dilution scenario: (a) transmission for initial absorbance $A_0 = 1.00$ and (b) original-sample Cu detection limits obtained by multiplying the two literature assay limits [5], [6] by D. Panel (b) uses a logarithmic vertical axis. Curves illustrate the stated equations, not wastewater measurements.

In this scenario, tenfold dilution increases incident-light transmission from 10.0% to 79.4%, while the copper detection limits become approximately 13.3 and 3603 µg L^{-1} on the original-sample basis. The optical advantage therefore comes with a concentration penalty. Transmission is shown as a physical indicator of attenuation; fluorescence collection has additional geometric and reabsorption dependencies [15], [16]. Actual matrix blanks and dilution-series measurements would establish whether a corresponding analytical improvement occurs.

This balance places a practical constraint on probe selection. A modestly sensitive probe may be adequate for a concentrated process stream but unsuitable after the dilution needed to suppress colour. A lower detection

limit can preserve sensitivity after dilution, yet strong ligands or adsorption to particles may still control the accessible metal fraction. The analytical decision should consequently be based on the complete sample-preparation and measurement procedure.

V. Implications for wastewater monitoring and pollution control

A useful optical method would connect molecular response with a defined monitoring question. At the inlet to a treatment process, the relevant task may be detecting a sudden change in metal loading. At the outlet, the task may be tracking a smaller residual concentration. These applications require different calibration intervals and may tolerate different degrees of dilution. The same hybrid should therefore be evaluated against the concentration range and matrix in which a decision will be made.

The strongest initial comparison is between the unsubstituted quinoline members and their 8-hydroxy analogues. If the hydroxyl-containing compounds exhibit stronger association but less discriminating responses, the result would indicate that increased affinity has not produced the required selectivity. A side-chain effect would be most informative when it improves aqueous handling without changing the signal through concentration-dependent aggregation. The two-variable design allows these possibilities to be examined without changing the entire chromophore at each step.

Monitoring and removal also remain separate chemical functions. The soluble probe is intended to measure a metal response in an analytical aliquot. The adsorption work of Li, Gao and Fang demonstrates how hydroxyquinoline groups can instead be immobilised in a material designed to retain metals [11]. Combining detection and capture would require a further material-development stage, with separate measurements of capacity, release, regeneration and leaching. For the present design, its contribution to pollution control would arise through better characterisation of influent, treatment response and residual metal fractions.

The principal unresolved issue is the relationship between conditional binding in the assay and metal availability in the original wastewater. Reference measurements, matrix-matched calibration and explicit fraction definitions provide a route to addressing it. A successful outcome would be reproducible agreement within a stated application range, together with an understood response when the sample falls outside that range. Such evidence would support subsequent development of a portable or immobilised format.

VI. Conclusion

The literature supports quinoline–carbazole hybrids as a chemically credible platform for investigating metal-ion detection. Retaining neutral quinoline nitrogen and introducing an 8-hydroxyl group provide a defined coordination strategy, while carbazole substitution offers a means of examining aqueous compatibility. The quantitative comparison shows that spectral displacement, quantum yield, absorption strength and detection limit describe different aspects of performance. Dilution further links optical clarity to the concentration sensitivity available in the original sample. The proposed QCH series should therefore be evaluated through matched structural comparisons and a matrix-specific analytical procedure supported by elemental spectrometry. This approach would establish whether the molecular response can provide useful information for industrial wastewater monitoring and treatment assessment.

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