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Selective Detector for Gas Chromatography Based on Adduct-Modulated Semiconductor Phololuminescence

by

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The photoluminescence (PL) of semiconducting n-CdS, Te-doped CdS, and CdSe can be used as the basis for a non-destructive, selective detector for gas chromatography. When placed in a series with the thermal conductivity detector (TCD) of a gas chromatograph, the semiconductor responds in parallel with the TCD to species that can engage in adduct formation: PL intensity is enhanced by Lewis bases like amines and quenched by Lewis acids such as carboxylic acids, relative to the intensity observed in the He carrier gas. Gases that interact more weakly with the semiconductor surface like hydrocarbons are not detected by the PL-based detector. For a n-CdS:Te detector, linear response regimes and detection limits have been determined as being ~0.1-3.0 μg and 0.1 μg for n-butylamine and ~0.2-1.5 mg and 0.2 mg for acetic acid.

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We have recently found that the photoluminescence (PL) of etched or cleaved n-CdSe, n-CdS, and Te-doped n-CdS (CdS:Te) single-crystal semiconductors is strongly affected by exposure to gaseous Lewis acids and bases at ambient temperature: acids like SO_2 caused a decrease in PL intensity while bases such as NH_3 and alkyl amines increased the intensity (1-3). Adduct formation at the gas-semiconductor interface is evidenced by correlations of the magnitude of the PL change, relative to a N_2 ambient, with intrinsic amine basicities and by the pressure dependence of the PL intensity, which can be fit to a Langmuir adsorption isotherm (2).

For etched CdSe samples, the PL changes appear to be driven by variations in the depletion width of the semiconductor resulting from adduct formation: our data fit a dead-layer model that is based on the assumption that electron-hole pairs formed within a distance on the order of the depletion width do not contribute to PL (4,5). The quantitative form of the model is given in eq 1.

$$PL_1/PL_2 = \exp(-\alpha'\Delta D) \qquad (1)$$

In this equation, PL_1 and PL_2 are the PL intensities in the presence and absence of the adduct-forming gas, ΔD is the corresponding change in dead-layer thickness (equated with the change in depletion width), and $\alpha' = (\alpha + \beta)$, where α and β are the absorptivities for the exciting and emitted light; this treatment assumes that the semiconductor's surface recombination velocity is either very large or insensitive to the change in gaseous ambient (5). The direction of the PL change corresponds to a shift in the work function of the semiconductor, moving it closer to the vacuum level for Lewis bases and farther from it for Lewis acids (2,6).

In principle, these observations can be exploited in the construction

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of a PL-based detector for gas chromatography (GC). We demonstrate in this paper that n-CdSe, CdS, and CdS:Te serve as nondestructive, selective, chromatographic detectors through their PL response to Lewis acids and bases capable of adduct formation with their surfaces.

EXPERIMENTAL SECTION

Materials. Single-crystal, vapor-grown, *c*-plates (10 x 10 x 1 mm) of undoped n-CdSe, n-CdS, and 100-ppm Te-doped CdS (CdS:Te) with resistivity of ~2 ohm-cm (4-point-probe method) were obtained from Cleveland Crystals, Inc., Cleveland, OH. The Te concentration is an estimate based on starting quantities. Samples were scored and broken to ~5 x 3 x 1-mm dimensions, alternately wiped and etched (Br_2/MeOH, 1:30 v/v; 5 s) until the shiny, Cd-rich, 0001 face was observed, ultrasonicated in MeOH for 15 min, and then glued in place with DUCO cement. Samples were left in air until use.

Apparatus. A semiconductor sample was mounted in a 15-mm long, 3-mm wide, square glass tube, tapered to fit over the exit port of a Gow Mac Model 150 gas chromatograph, as shown schematically in Figure 1. A standard 1/4" x 6 ft Carbowax 20M column with helium carrier gas was employed. The instrument's thermal conductivity detector (TCD), operated at 250°C, served as one detector. The emissive semiconductor, connected in series and separated from the TCD by a flow time of a fraction of a second, served as a second detector. The semiconductor was either used at ambient temperature or was heated by placing the tube containing the semiconductor in contact with an aluminum block that was heated to 80°C. Irradiation sources for semiconductor excitation included a 5-W Coherent Radiation Model Innova 90 Ar^+ laser (457.9 and 514.5 nm) and a 10-mW Melles Griot Model 80 He-Ne laser (632.8 nm). Laser plasma lines were eliminated by passing the laser beams through Oriel interference filters (fwhm of 10 nm, centered at the laser line). The beam was then passed through a 10-X beam expander and masked to illuminate only the semiconductor surface. Laser intensity was measured with a Coherent Model 212 power meter and corrected for spectral sensitivity. The illumination intensity was typically 5 mW/cm^2. Uncorrected, low-resolution (~3 nm) PL spectra were obtained with a McPherson Model 270, 0.35-m monochromator, equipped with a grating blazed at 500 nm, a R928 PMT, and an EG&G ratemeter; laser excitation was filtered by placing a Corning 2-71 filter at the entrance slit to the emission monochromator. The PL signal was brought to the spectrometer using a 3-mm diameter optical fiber. PL intensity was monitored by sitting at the band maximum (~510-nm edge emission for CdS and CdS:Te; ~600-nm Te-based subband gap emission for CdS:Te(7); and ~720-nm edge emission for CdSe) with the recorder operated in time-base mode as the chromatogram was recorded.

Procedure. Samples of 0.2-5.0 µL were injected into the gas chromatograph using a 10 µL Hamilton syringe. For concentration studies, some samples were first diluted with hexane in 100 mL volumetric flasks. The gas chromatograph was operated, depending on the sample, from 100-150°C and with He carrier gas flow rates, measured with a soap-bubble flowmeter, of 70-100 mL/min. Chromatograms were recorded from the dual detectors on separate chart recorders.

RESULTS AND DISCUSSION

As illustrated in Figure 1, the change in band edge (CdS, CdS:Te, and CdSe) or subband gap (CdS:Te) PL intensity can be monitored in series with the response of a gas chromatograph's thermal conductivity detector (TCD). In sections below we describe the nature of the PL response, its selectivity, and its concentration dependence.

PL Response. Our initial studies were carried out with n-butylamine. The magnitude of the PL enhancement induced by the amine is shown relative to the PL intensity in He in Figure 2. The actual percentage increase with n-butylamine is typically on the order of 10 - 50% for any of the II-VI semiconductors employed. Since semiconductor absorptivities generally increase with photon energy, eq 1 predicts that shorter excitation wavelengths should magnify the PL increase. However, a trade-off arises because the PL signal-to-noise ratio usually declines with shorter excitation wavelengths. We have found that good responses can usually be obtained using an Ar^+ laser (CdS, CdS:Te, CdSe) or with an inexpensive He-Ne (CdSe) laser for excitation.

Figure 3 presents a dual chromatogram obtained with multiple injections of n-octylamine. Most striking is the parallel response of the TCD and the PL detector. The PL peaks tend to be broadened relative to those of the TCD: a sharp rise is generally seen as the gas reaches the semiconductor, but reversal of the PL change is more sluggish. The reversal is more rapid when the semiconductor is heated.

The PL intensity is sensitive to the ambient temperature: As the ambient temperature is increased, the absolute PL intensity decreases. Therefore, in order to maintain a constant baseline, the temperature must be stable. We also find that the relative PL detector response decreases at higher temperature, presumably reflecting smaller adduct formation constants. For example, 1 µL injections of ethyl alcohol or dibutyl ether elicit weak responses when a CdS:Te detector is at 30°C, but no responses, within experimental error, at 80°C.

The stability of the PL detectors over time is generally good. However, as was noted earlier (1-3), we sometimes find that the first use of a freshly etched sample yields a PL response that differs from the reproducible response that is subsequently observed with repeated injections. The uniformity of the PL excursions is roughly comparable to that of the TCD, as illustrated in Figure 3. We have used a single semiconducting sample as a detector for as long as two months without re-etching; no deterioration in response was observed over that period.

Selectivity. The PL detector exhibits a selectivity to volatile species that correlates with their Lewis acidity and basicity. Figure 4 reveals that Lewis bases like methanol, n-butylamine, pyridine, triethylamine and 2-propanethiol cause PL enhancements. In contrast, Figure 5 shows that a reduction in PL intensity is found when a carboxylic acid, acetic acid, is present. Interestingly, no isotope effect is seen within experimental error when perdeuterated acetic acid is used, as also shown in Figure 5. Representative alkanes, alkenes, alkynes, alkyl halides, aromatic hydrocarbons, nitriles, ketones, and esters gave no response within experimental error (2).

Selectivity was directly demonstrated using a multicomponent sample. As shown in Figure 6, the TCD responds to all of the indicated gases, but the PL detector responds only to those gases that, by virtue of their strong Lewis basicity, readily form adducts with the semiconductor. In this sense the PL detector complements the TCD through its ability to identify peaks as arising from Lewis acids or bases.

Concentration Dependence. The magnitude of the PL response was investigated in more detail with *n*-butylamine and acetic acid. At high concentrations, the response saturates: Figure 3 illustrates this effect for *n*-octylamine, showing that an increase in the amine quantity from 1.5 to 2.0 µL does not further increase the PL intensity. We do find regimes of linear response, however. For *n*-butylamine, the PL enhancement is linear from ~0.1 to 3.0 µg, and for acetic acid, linearity in PL quenching is found from ~0.1 to 1.5 mg; these ranges should be treated as approximate since they are detector dependent. The useful working range can be extended above these concentration limits by constructing calibration curves.

The minimum quantity of material that we have detected using the PL methodology is ~0.1 µg, corresponding to a 1.0 µL injection of a 0.0100% *n*-butylamine solution in hexane. The detection limit for acetic acid is significantly poorer, ~0.1 mg. This variability in response is another illustration of the chemically specific interactions taking place at the semiconductor-gas interface. In principle, the use of other emissive semiconductors, having different steric and electronic surface landscapes, can increase the versatility of this detection system. Such studies are presently in progress in our laboratories.

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Figure Captions.

Figure 1. Schematic of the detection system. GC and SC are the gas chromatograph and semiconductor. The two outputs shown are those of the thermal conductivity detector and the semiconductor's PL intensity.

Figure 2. The initial PL spectrum of a CdS:Te detector. Superimposed are the changes in PL intensity at 600 nm, using the apparatus of Figure 1, resulting from repetitive exposure of the etched CdS:Te sample in He (initial response) to 1-μL injections of n-BuNH$_2$. Conditions: heated n-CdS:Te detector; 458-nm excitation; 600-nm emission; He flow rate, 100 mL/min; oven temperature, 100°C.

Figure 3. Parallel response, using the apparatus of Figure 1, of the thermal conductivity detector (TCD) and the PL detector to the indicated quantity of n-octylamine. Conditions: heated n-CdS:Te detector; 458-nm excitation; 515-nm emission; He flow rate, 100 mL/min; oven temperature, 150°C.

Figure 4. Repetition of the experiment described in Figure 3, using the indicated compounds. Each peak represents the injection of 1.0 μL of the neat liquid with the exception of MeOH where 5 μL was used. Conditions: heated n-CdS:Te detector; 458-nm excitation; 515-nm emission; He flow rate, 70 mL/min; oven temperature, 100°C.

Figure 5. Repetition of the experiment described in Figure 3, using the indicated carboxylic acids. Each peak represents the injection of 1.0 μL of

the neat liquid. Conditions: ambient n-CdS:Te detector; 458-nm excitation; 600-nm emission; He flow rate, 100 mL/min; oven temperature, 150°C.

Figure 6. Repetition of the experiment described in Figure 3, using a multicomponent sample of the indicated species. Conditions: ambient n-CdS:Te detector; 458-nm excitation; 600-nm emission; He flow rate, 70 mL/min; oven temperature, 100°C.

BRIEF

The photoluminescence intensity of n-CdS and n-CdSe is affected by exposure to volatile Lewis acids and bases, permitting the construction of a nondestructive, selective detector for gas chromatography.

CREDIT

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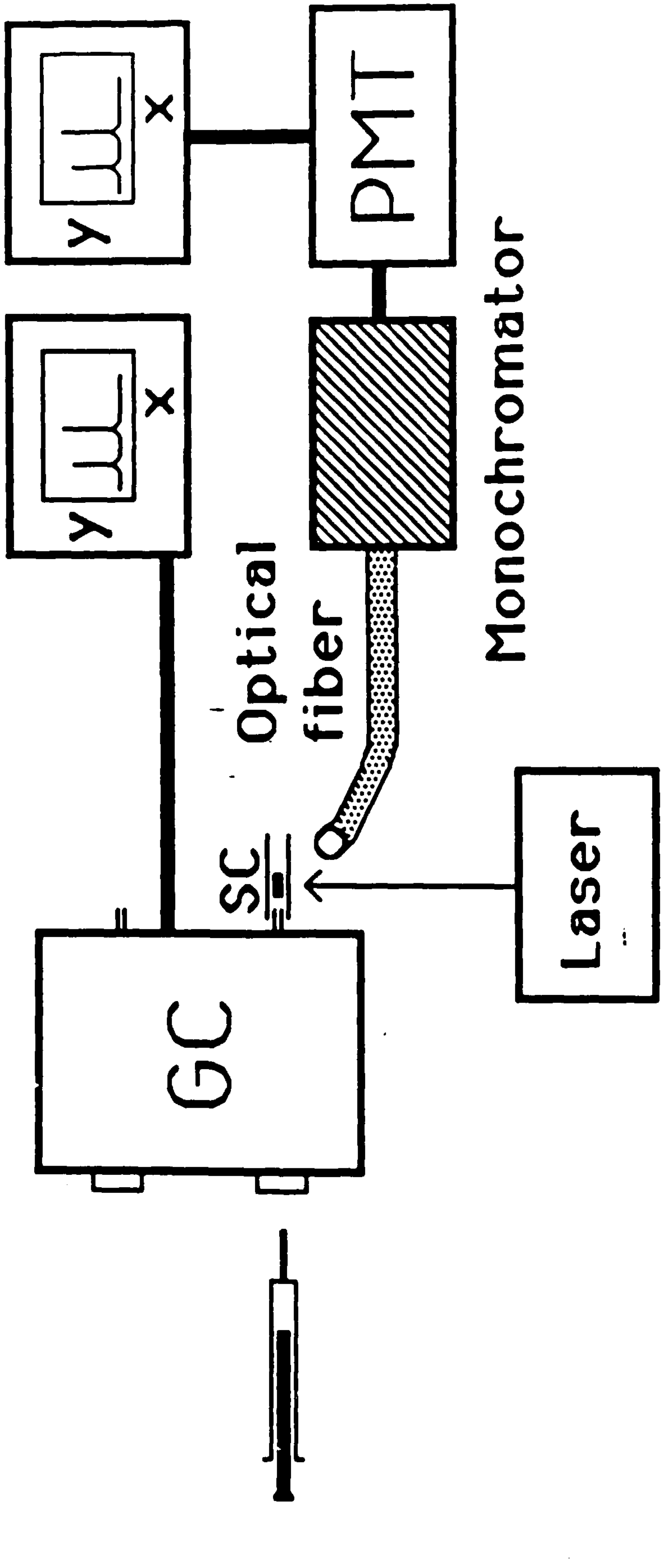
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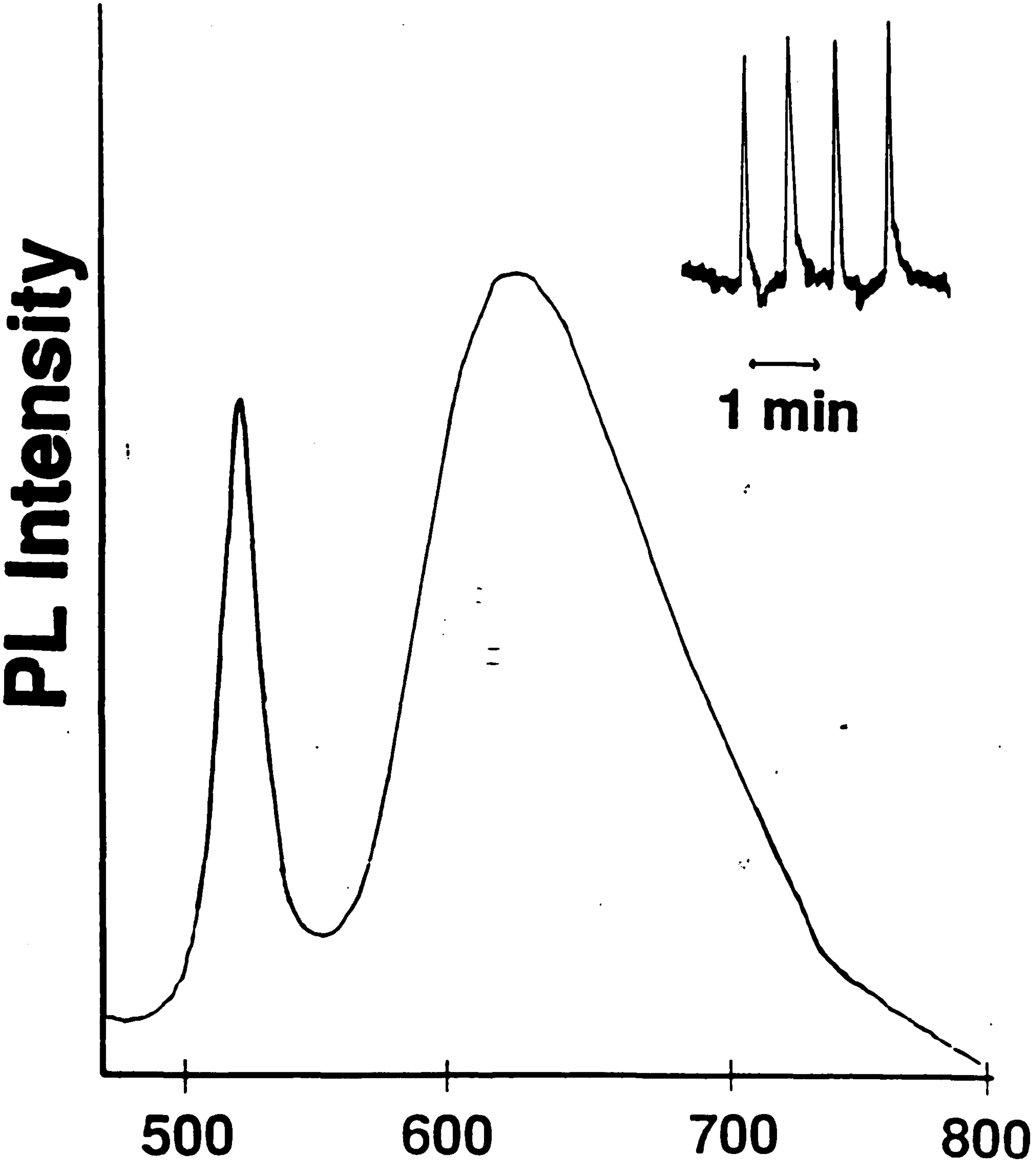
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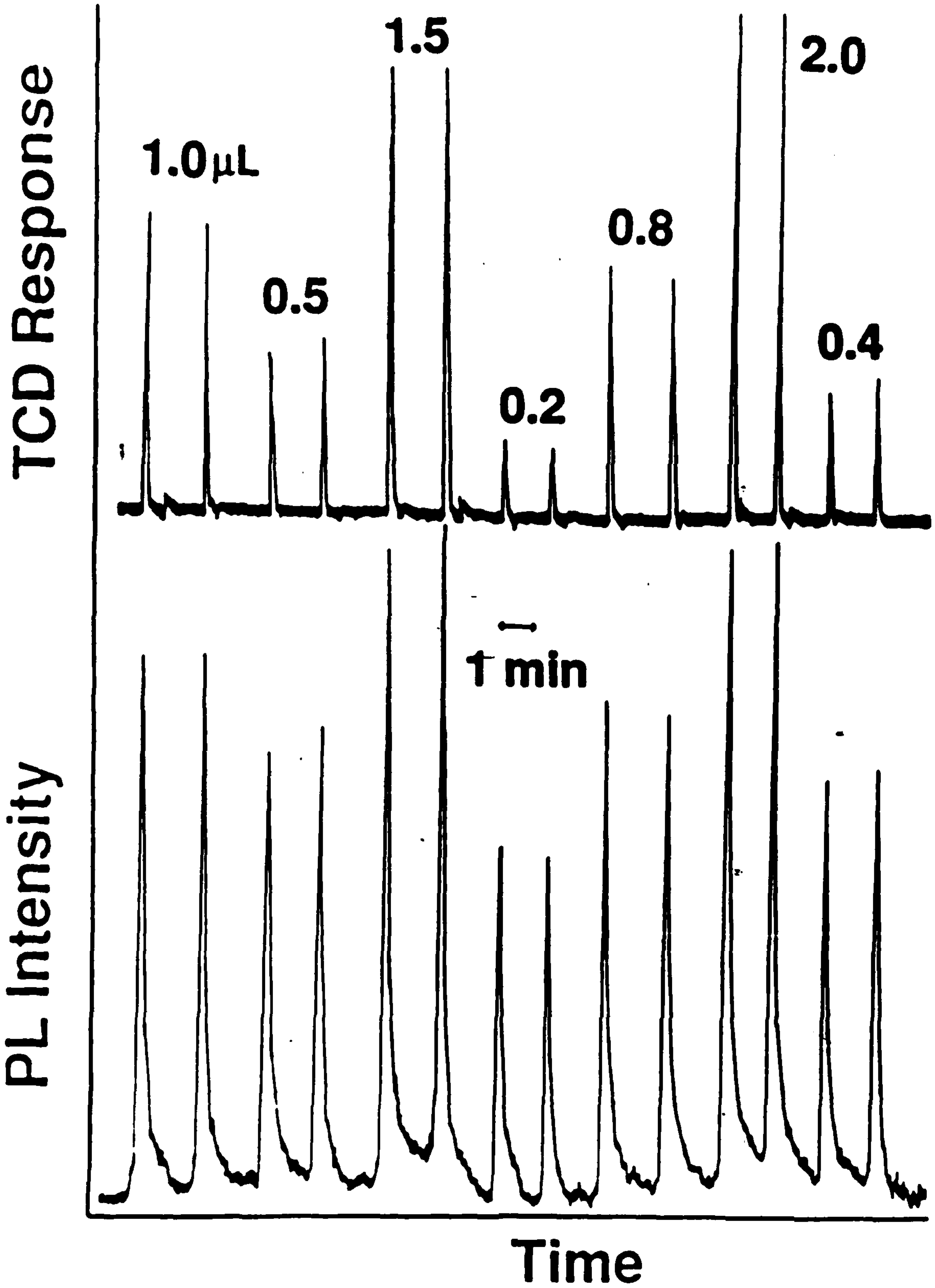
800
Wavelength, nm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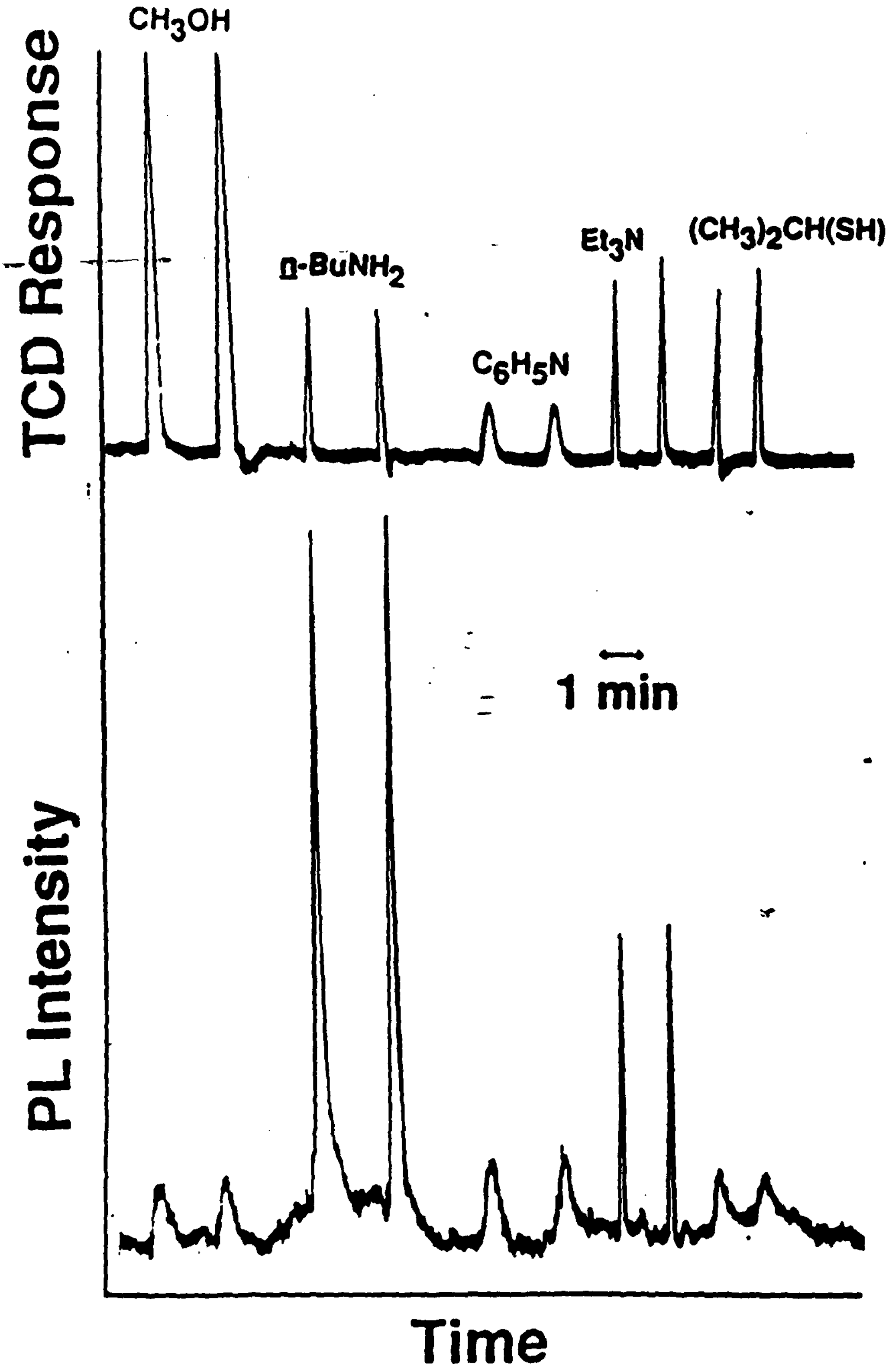
1.5
0.2
0.8
2.0
0.4
1 min
PL Intensity
Time



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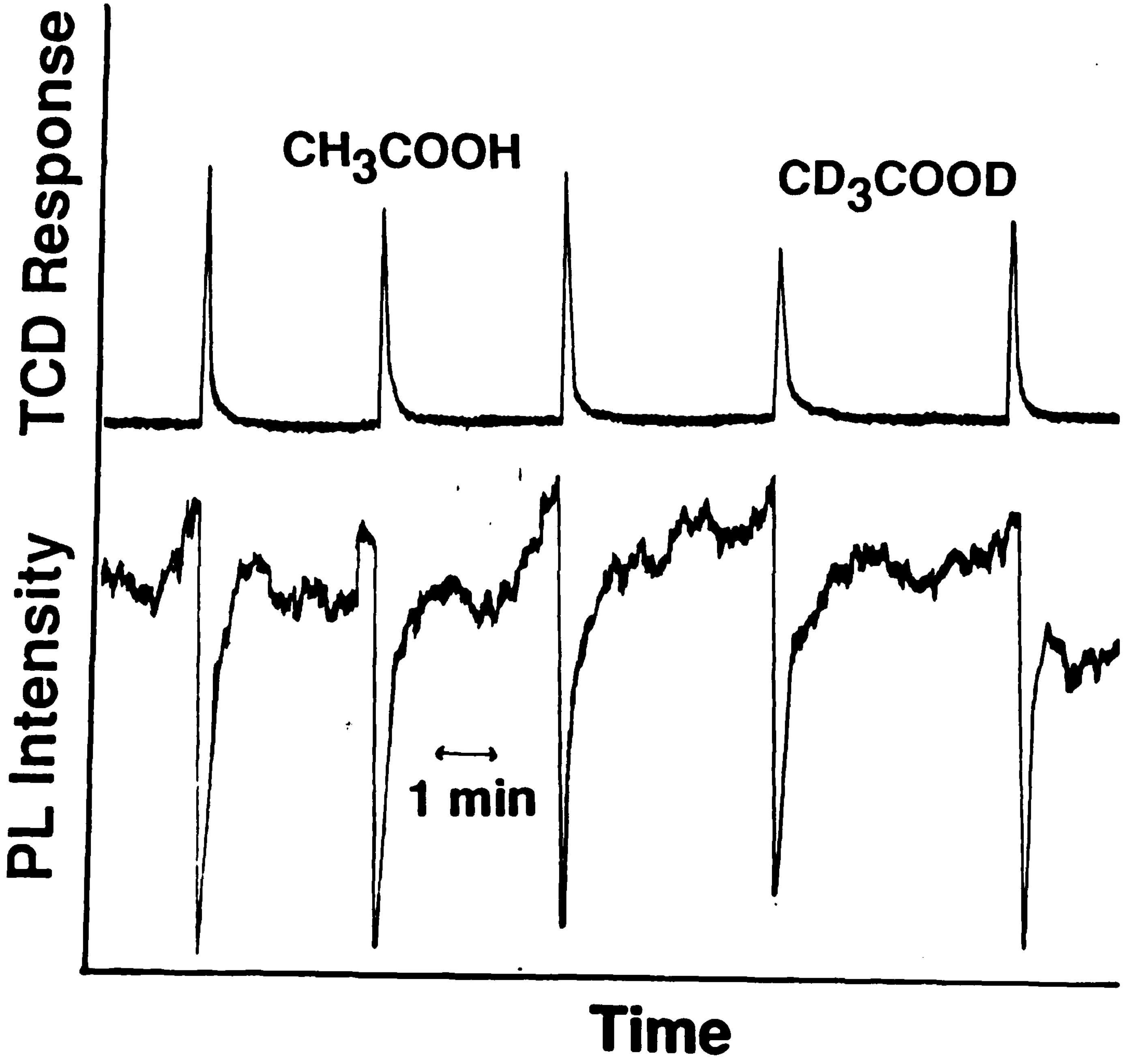
TCD Response
1 min
PL Intensity
Time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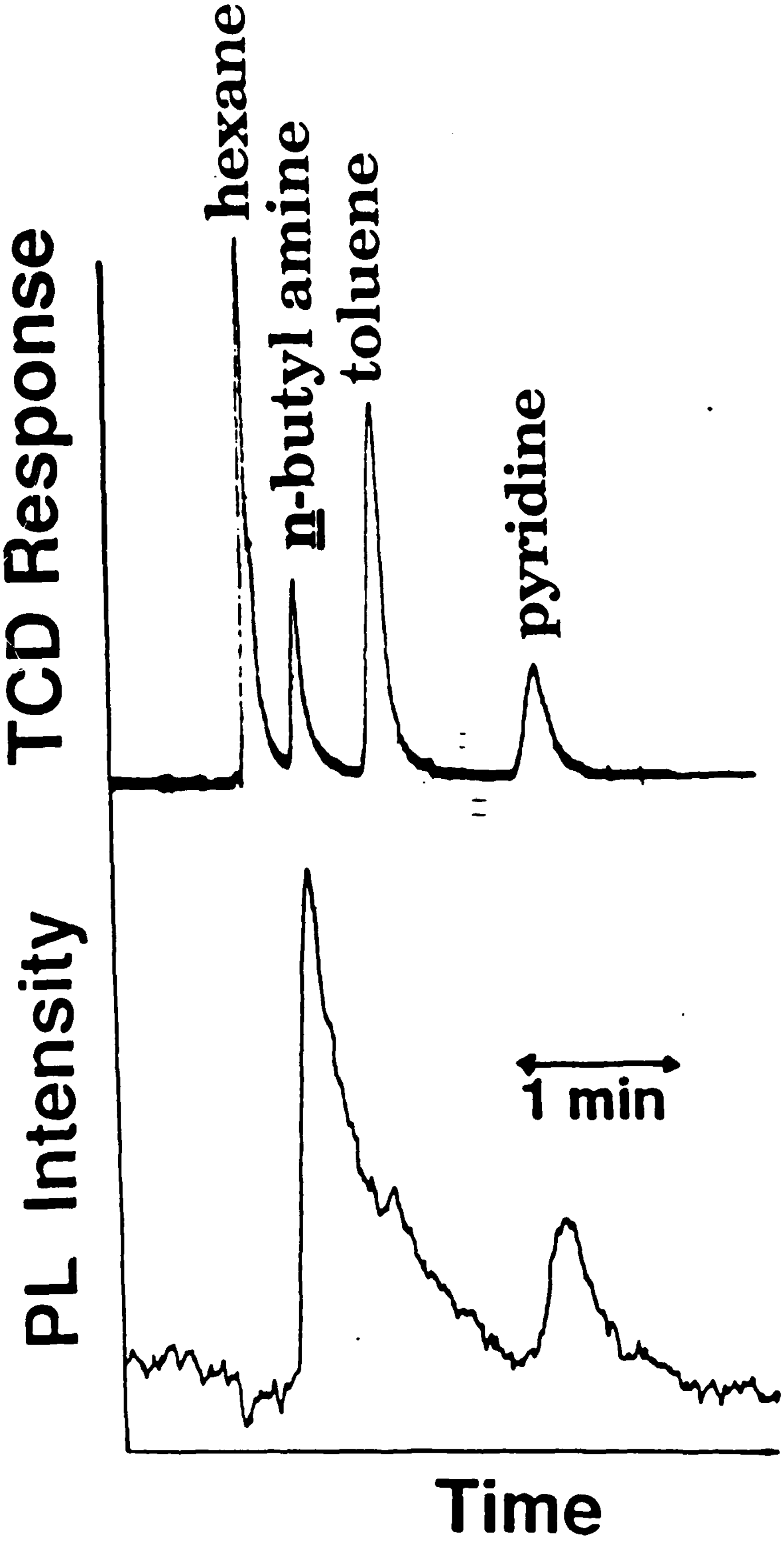
CD_3COOD
1 min
Time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toluene
pyridine
PL Intensity
1 min
Time