Chiral Functionalization of Optically Inactive Monolayer-Protected Silver Nanoclusters by Chiral Ligand-Exchange Reactions

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•0.5 mmol of $AgNO_3$ dissolved in water (0.121 M)+ 0.5 mmol of penicillamine were at first mixed in methanol (100 mL),+ freshly prepared 0.2M aqueous $NaBH_4$ solution(25 mL) under vigorous stirring.

•The precipitate was then thoroughly washed with ethanol.

• Nanocluster powder was obtained by a vacuum-drying procedure.

• In the syntheses, they used five kinds of penicillamine with different ee values: (i) *rac*-Pen (0%ee), (ii) pure D-Pen (100% ee of D-isomer), (iii) pure L-Pen (100 ee of L-isomer), (iv) mixture of D-/L-Pen at a molar ratio of 3:1 (50%ee of D-Pen), and (v) mixture of D-/L-Pen at a molar ratio of 1:3 (50% ee of L-Pen).

•The reaction was conducted by stirring an aqueous solution (1.0 mL) of the as-synthesized *rac*- Pen-protected silver nanocluster powder (10.0 mg) and enantiopure D- or L-Pen (5.0 mg) overnight at room temperature under an inert,(N_2-saturated) atmosphere. The uncapped optically active penicillamine residue could be excluded by polyacrylamide gel electrophoresis (PAGE)

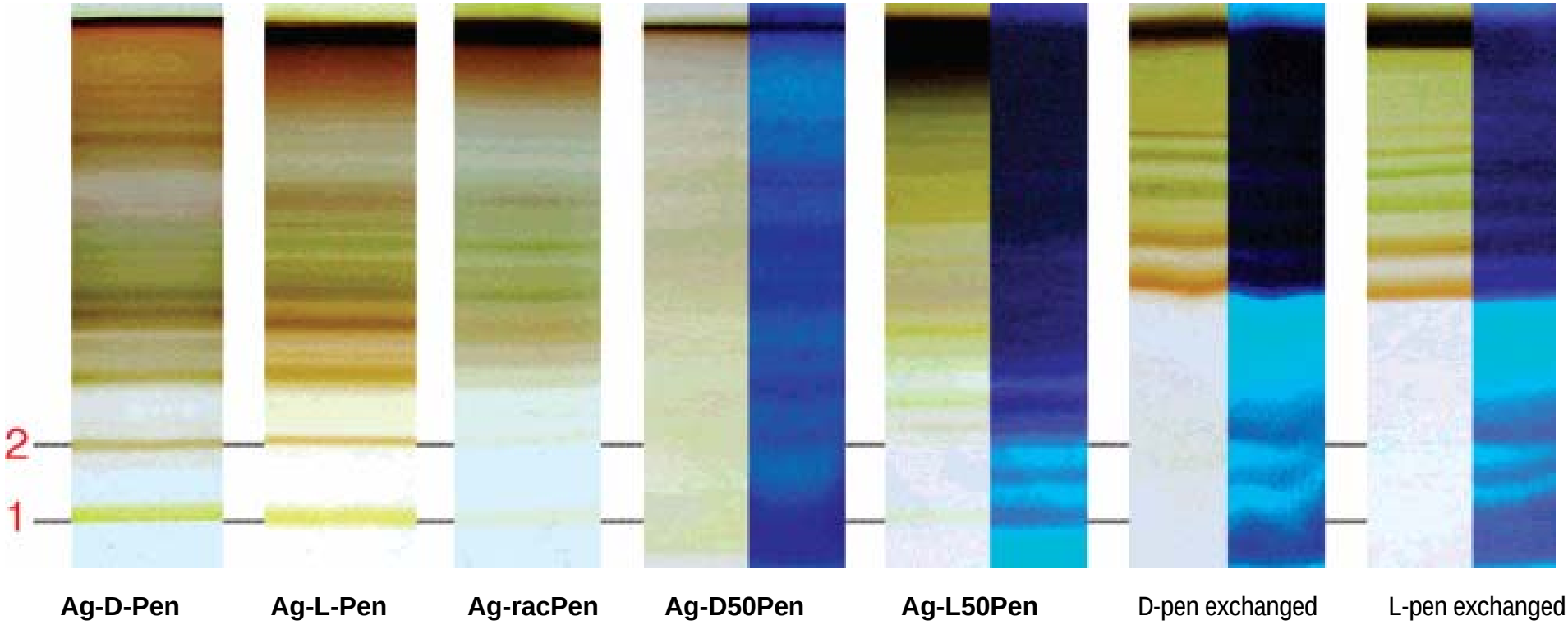


Fig 1.Photographs of the PAGE separation. Bands 1 and 2 are common in all samples: (i) Ag-D-Pen, (ii) Ag-L-Pen, (iii) Ag-*rac*-Pen, (iv) Ag-D50-Pen, (v) Ag-L50-Pen, (vi) D-Pen ligand-exchanged sample, and (vii) L-Pen ligandexchanged.

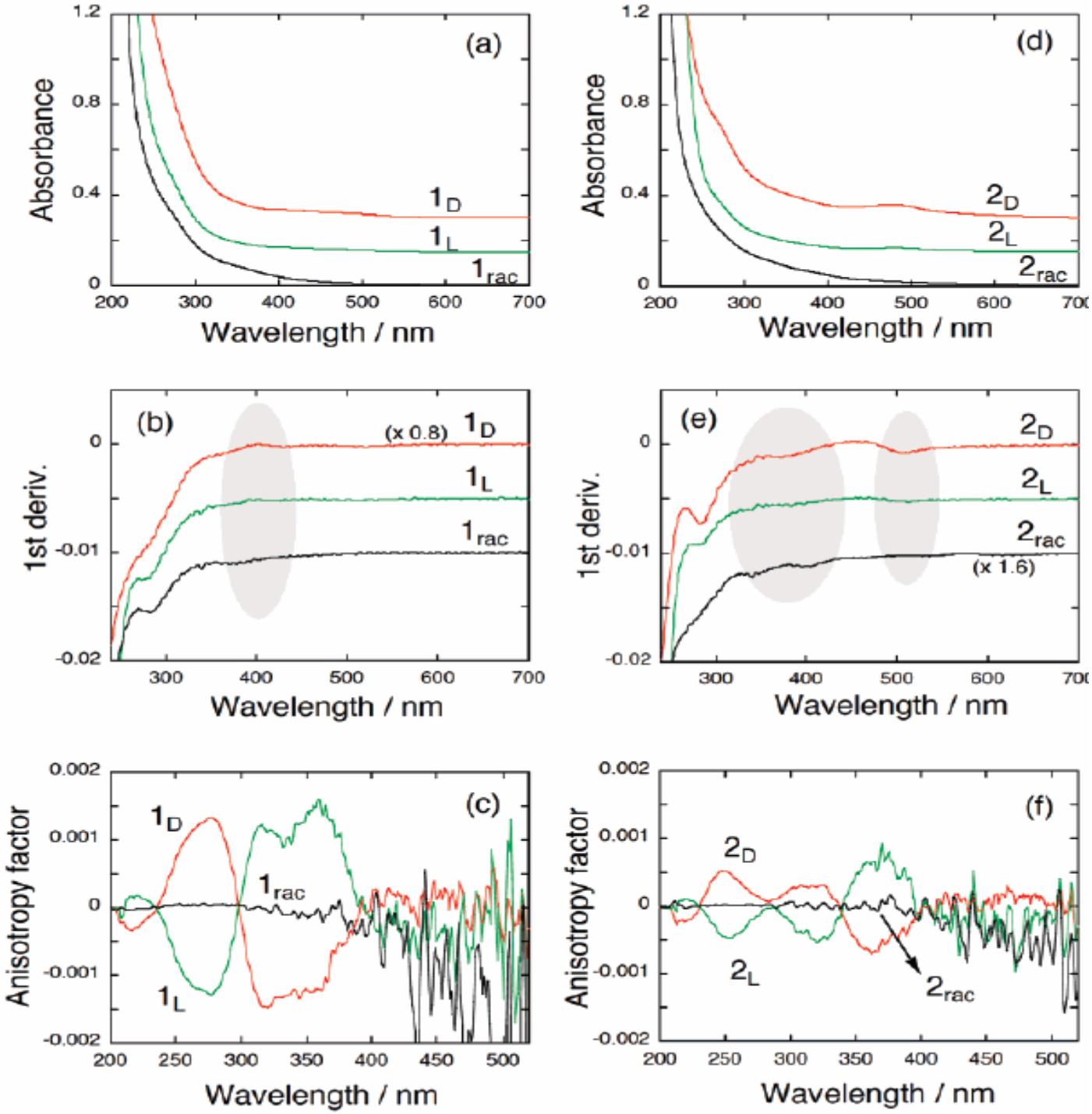


Fig 2. a-c d-f shows absorption spectra, first derivative spectra, and anisotropy factors of 1D/1L/1rac, and 2D/2L/2rac, respectively.

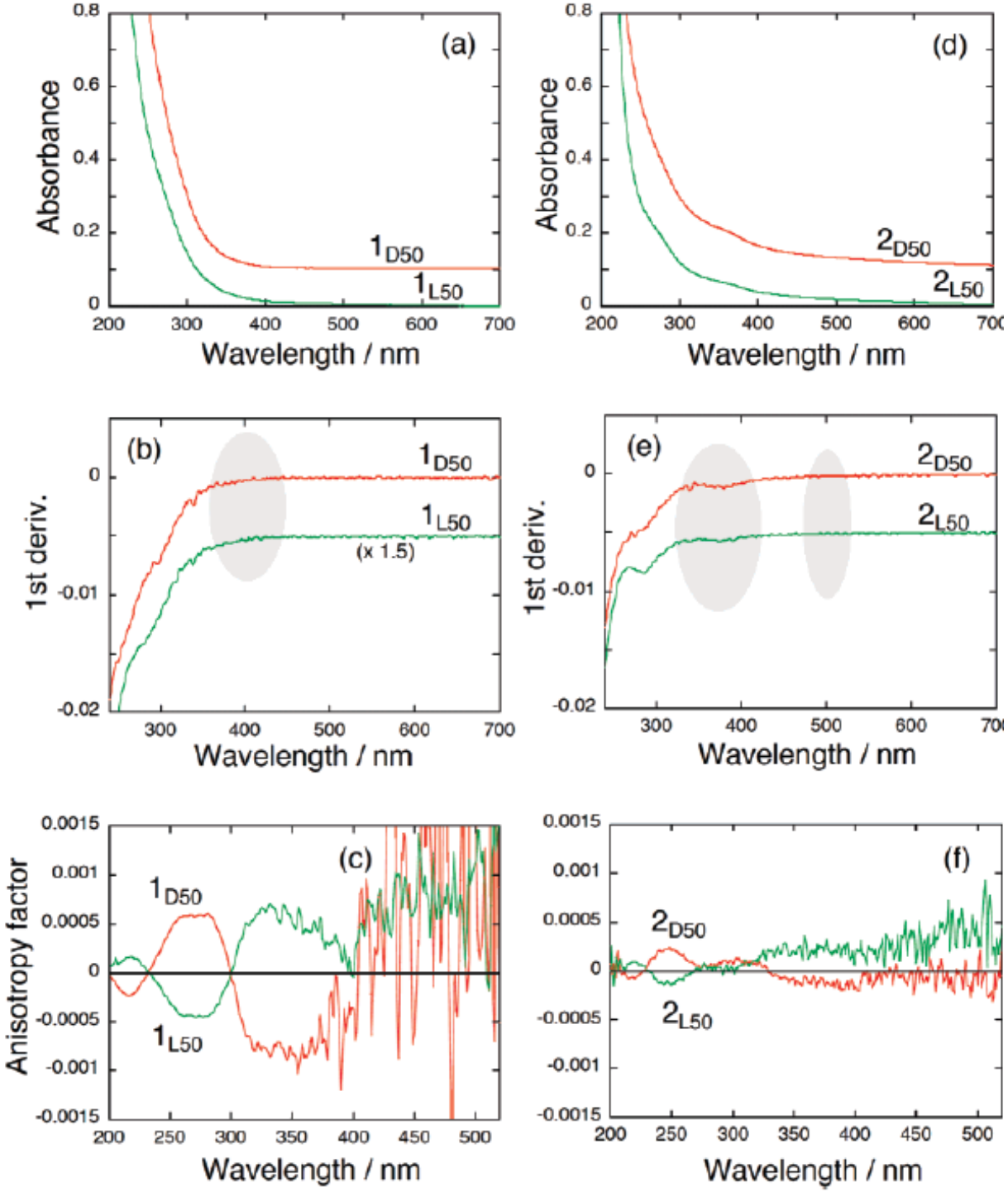


Figure 3. Panels a-c d-f shows absorption spectra, first derivative spectra, and anisotropy factors of 1D50/1L50,and 2D50/2L50 respectively.

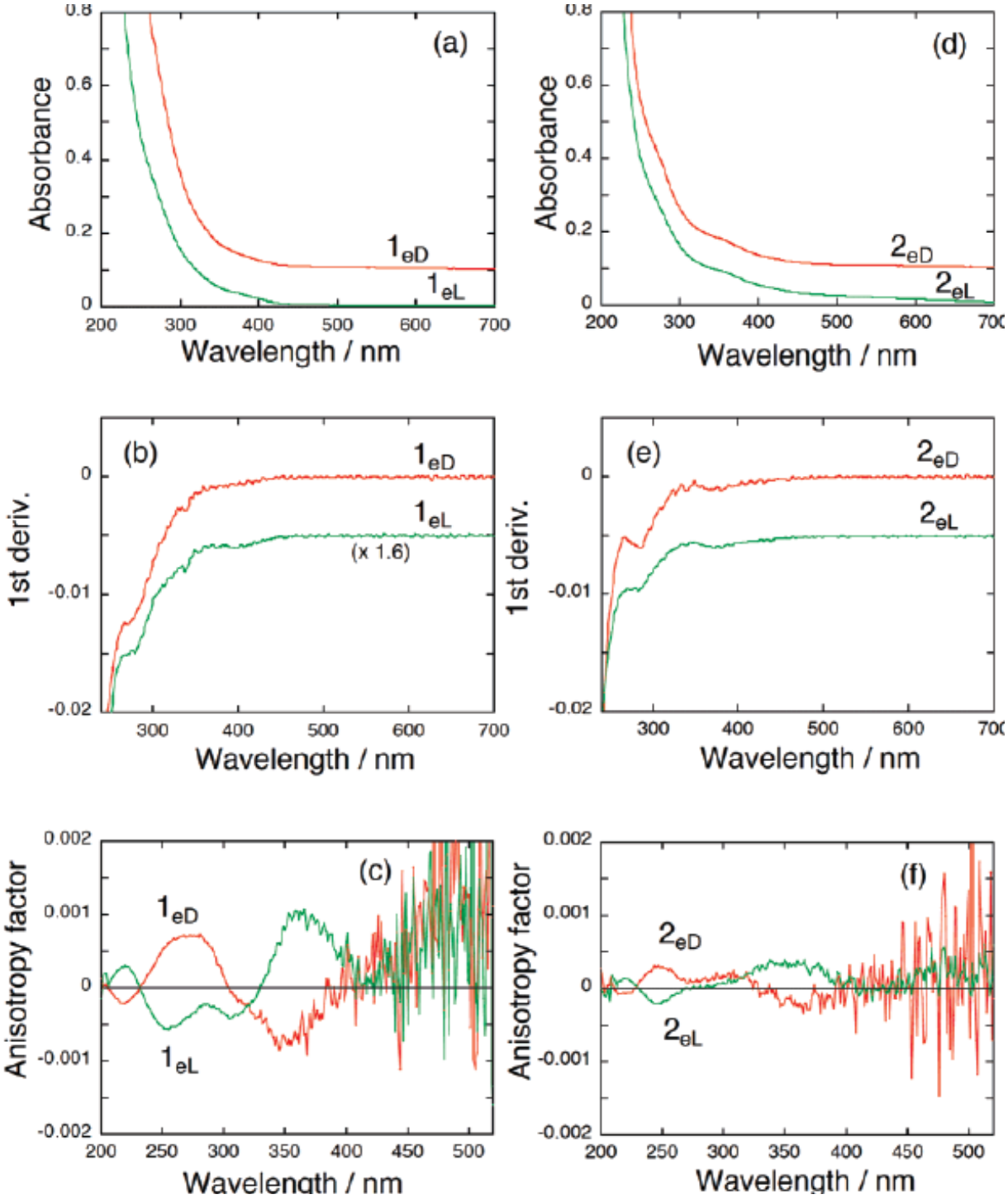


Figure 4. Panels a-c, d-f shows absorption spectra, first derivative spectra, and anisotropy factors of 1eD/1eL, and 2eD/2eL, respectively.

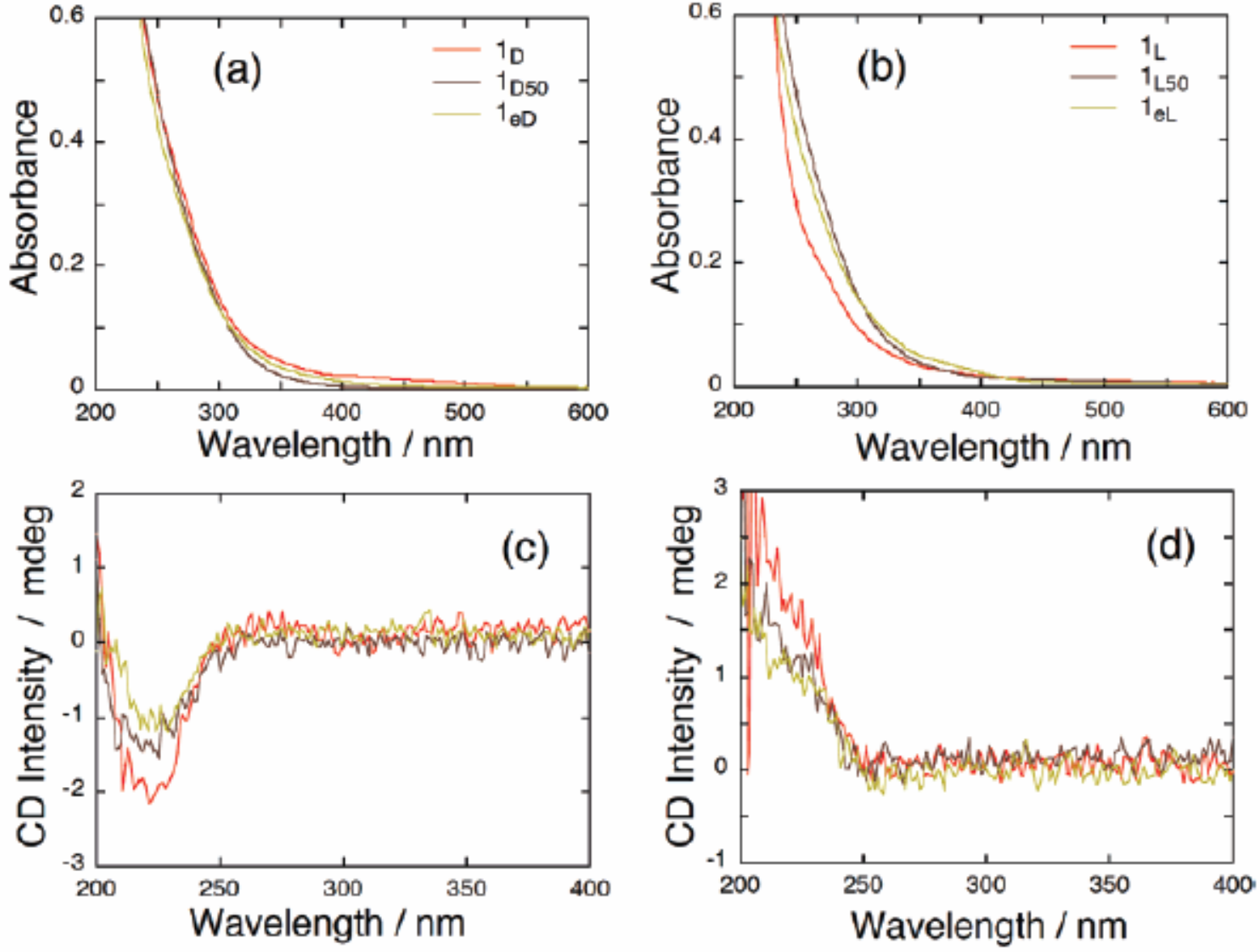
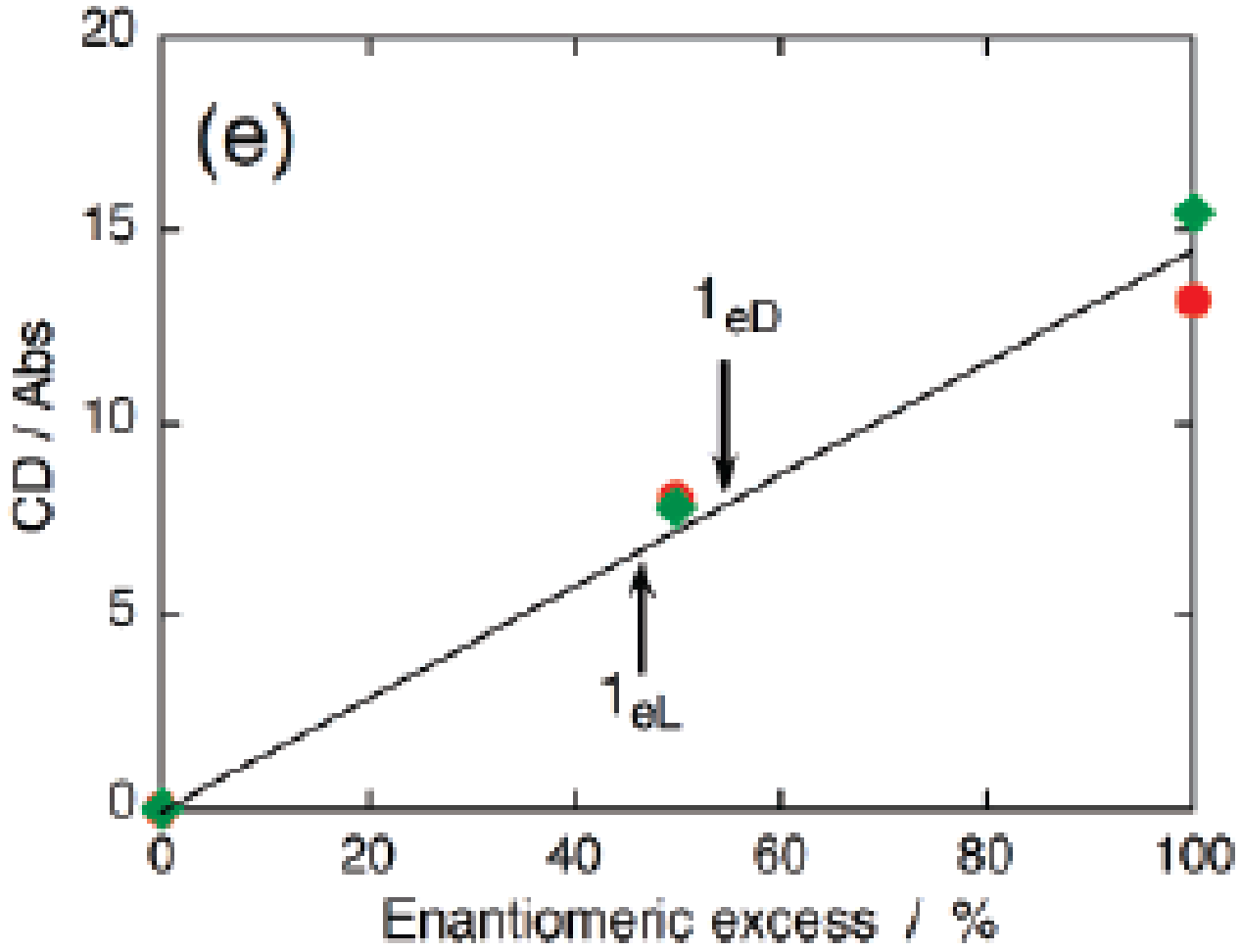


Fig 5. Panels a and b show absorption spectra of 1D/1D50/1eD and 1L/1L50/1eL before acidification (acid-untreated samples). Panels c andd show CD spectra of the respective compounds after acidification.



(e) Relationship between the initial ee value of the surface ligand and the CD signal intensity (averaged at 225-230 nm)

1. The ligand-exchange reaction between the optically inactive racemic penicillamine monolayer on a silver nanocluster surface by enantiopure D- or L-penicillamine.

2. The ligand-exchanged nanoclusters displayed a different PAGE separation pattern from that of the normally synthesized samples.
3. The emergence of the identical band positions in the separating gel assured the presence of size-invariant nanoclusters (1.05 and1.30 nm in core diameter) and allowed us to investigate the optical/chiroptical properties of these nanoclusters
4. The ligand-exchange experiments as well as the normal syntheses of the silver nanoclusters revealed that their absorption profiles and anisotropy factors were strongly dependent on the enantiomeric purity (or enantiomeric excess) of surface chiral penicillamine
5. The larger optical activity as compared to that of the analogous gold nanoclusters with a comparable size might be due to the silver core deformation or rearrangement