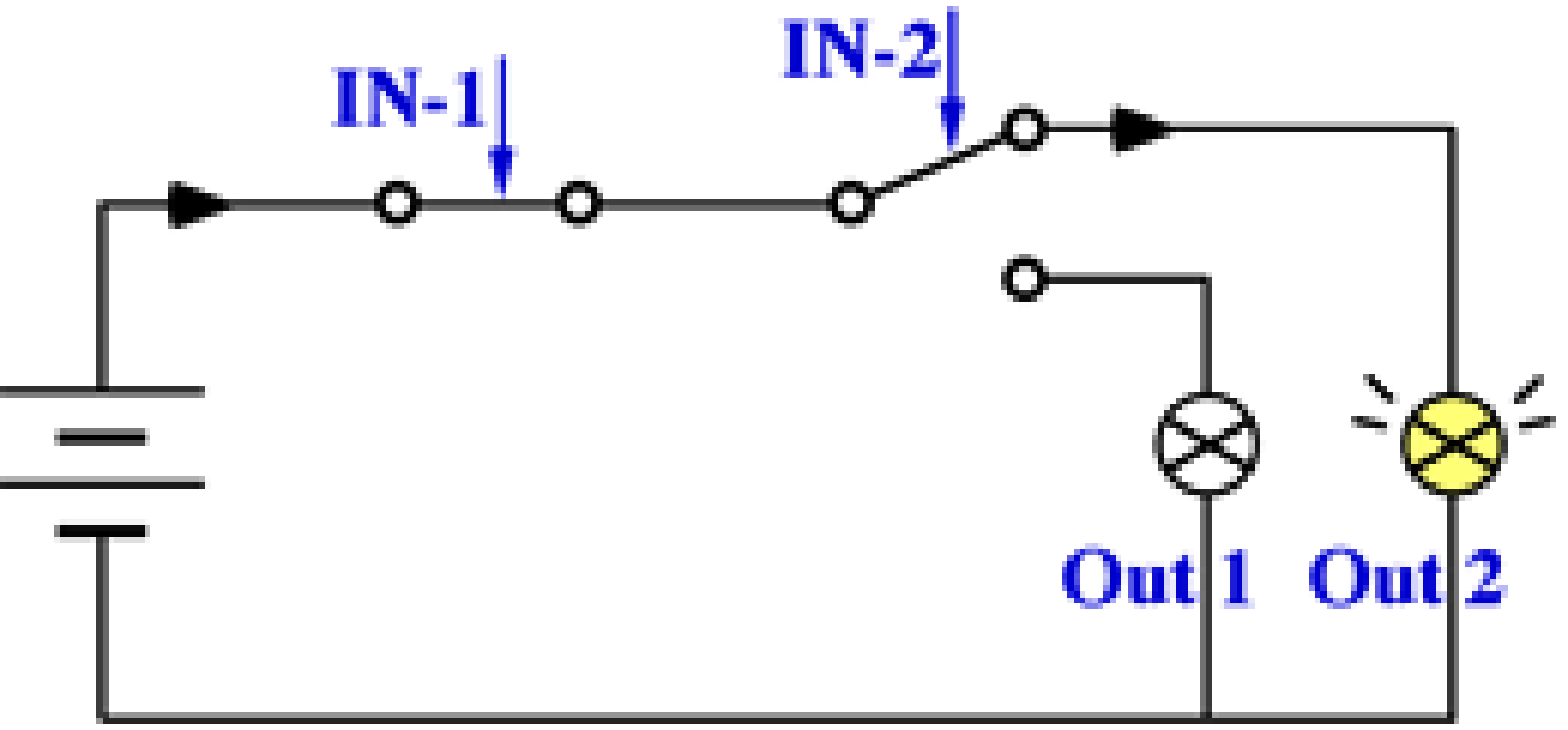
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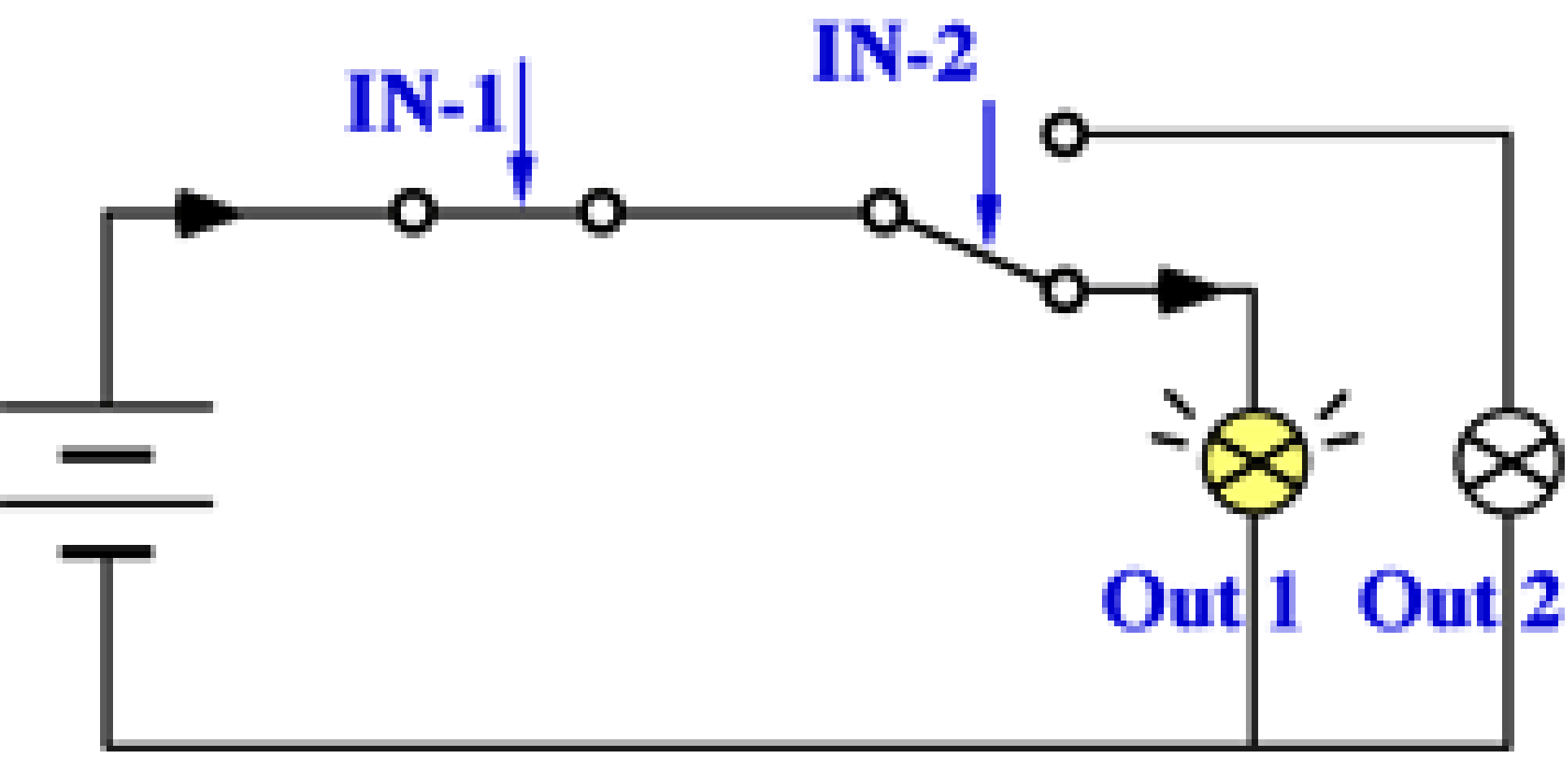
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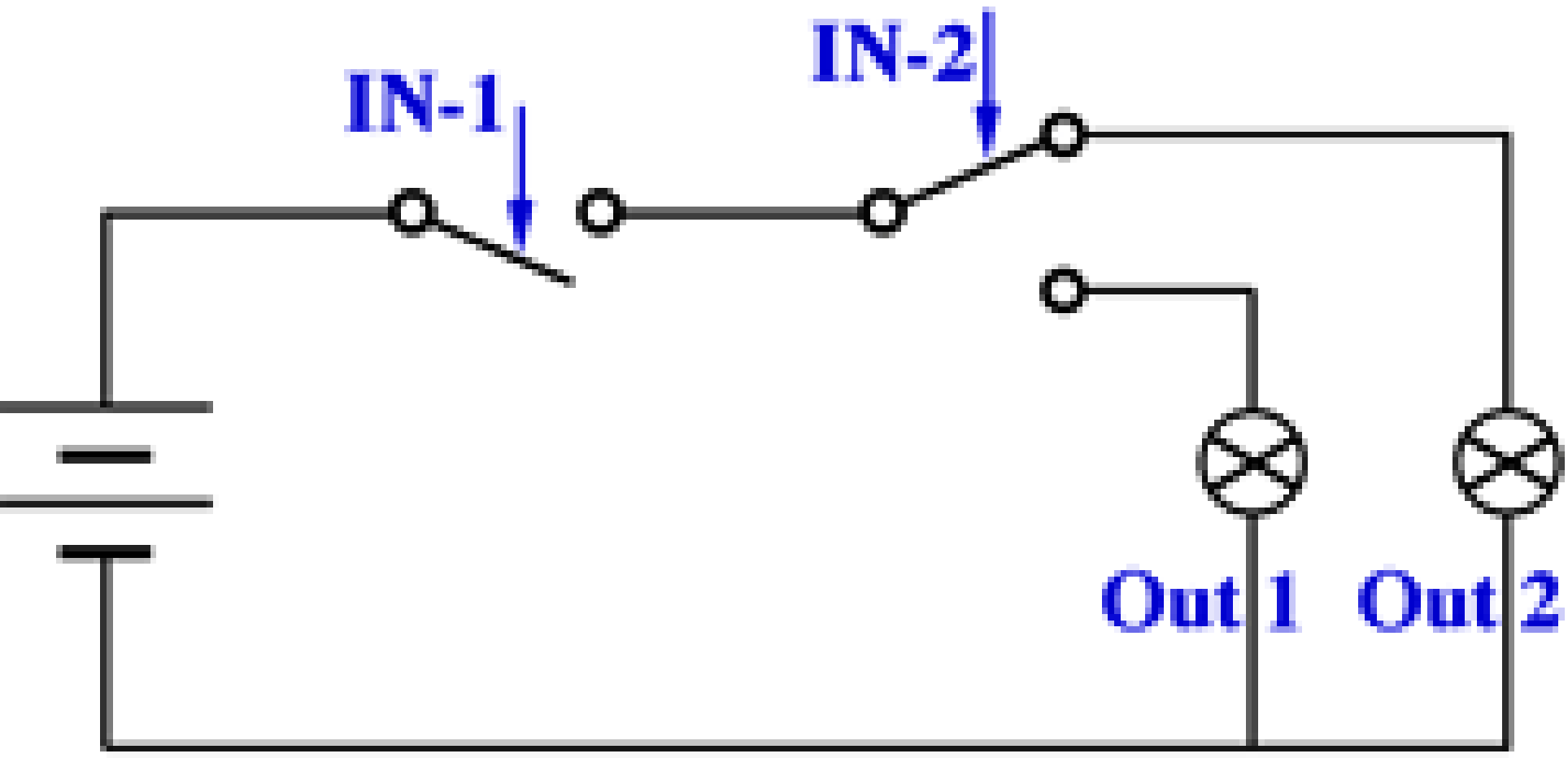
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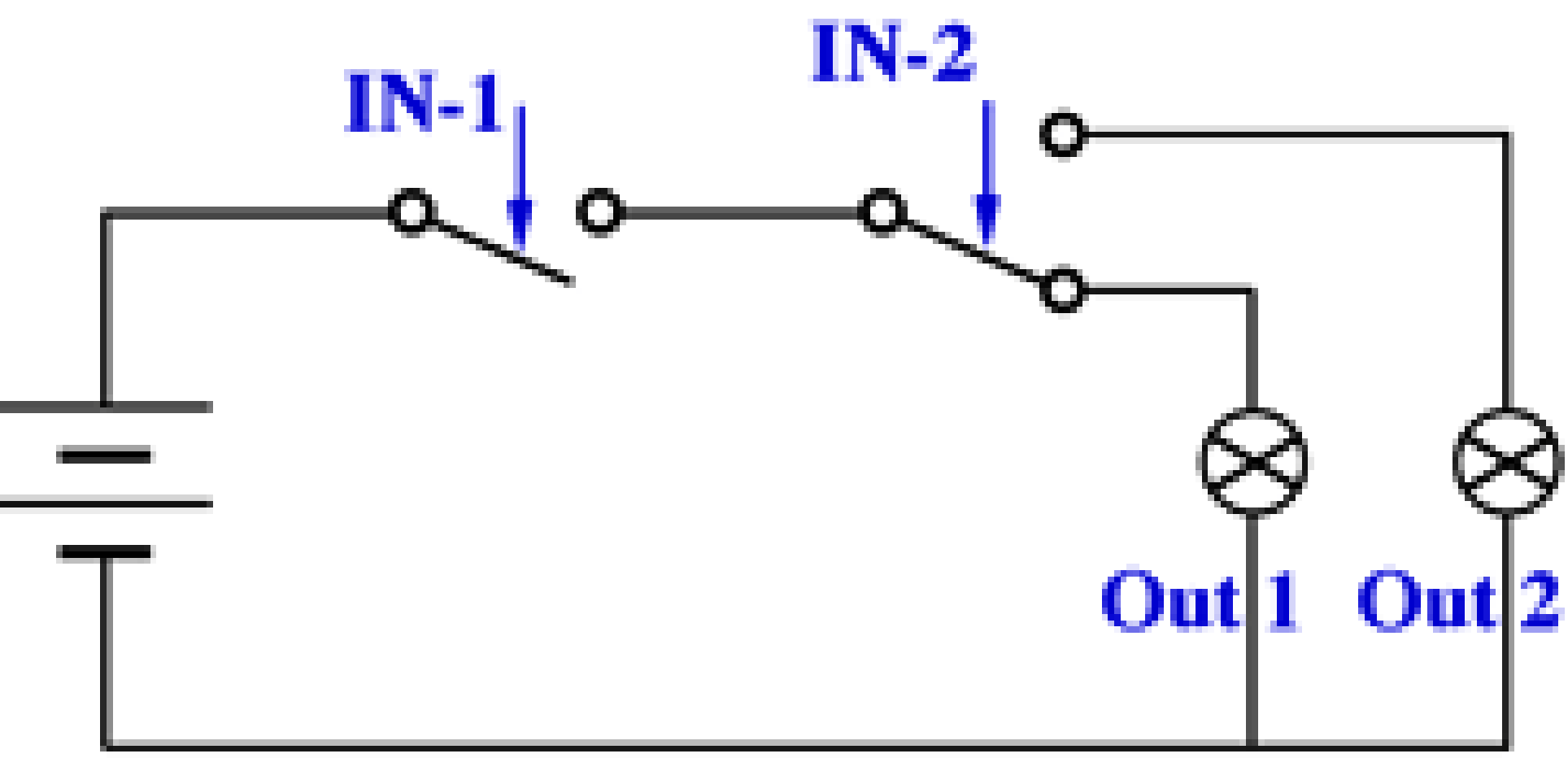
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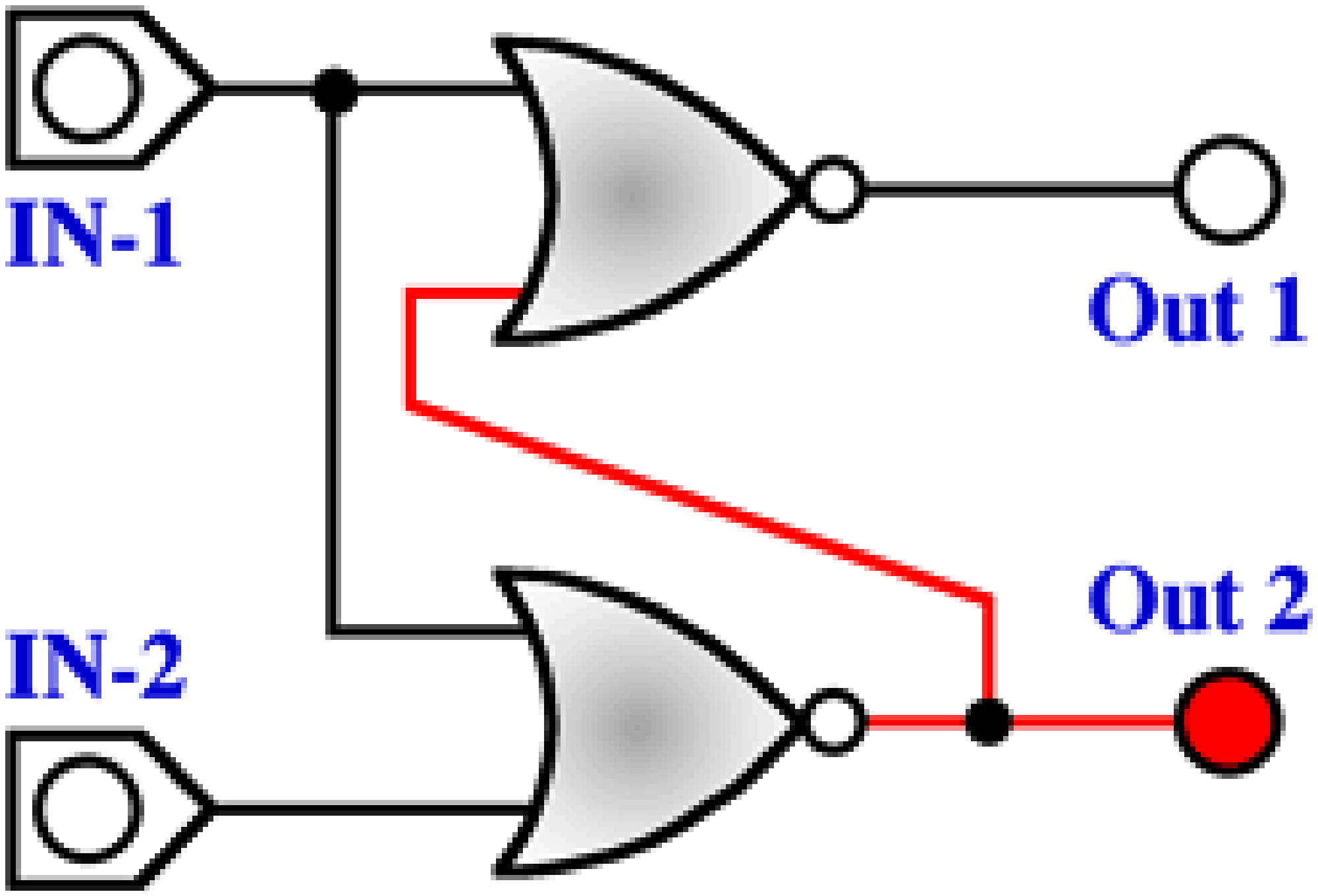
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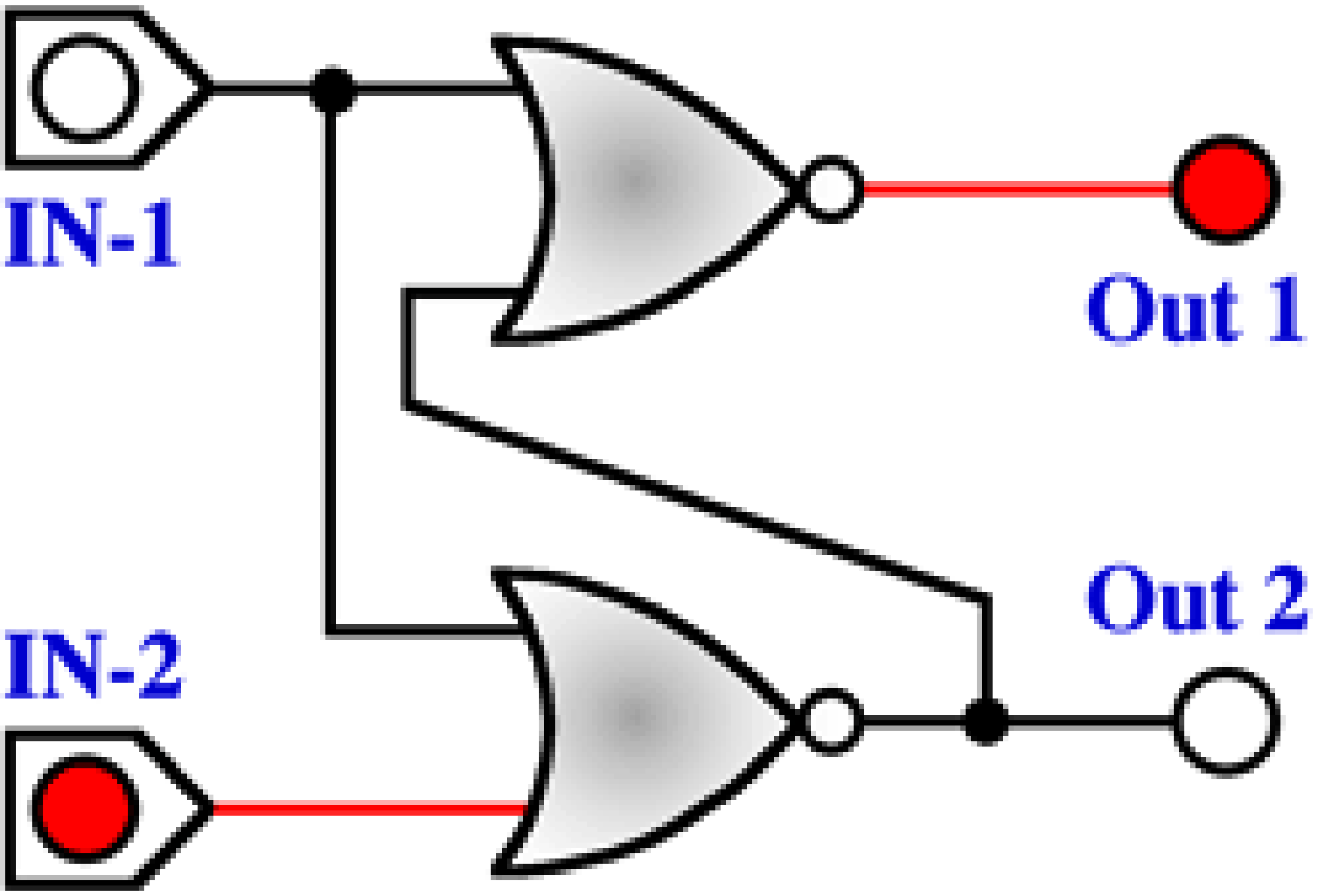
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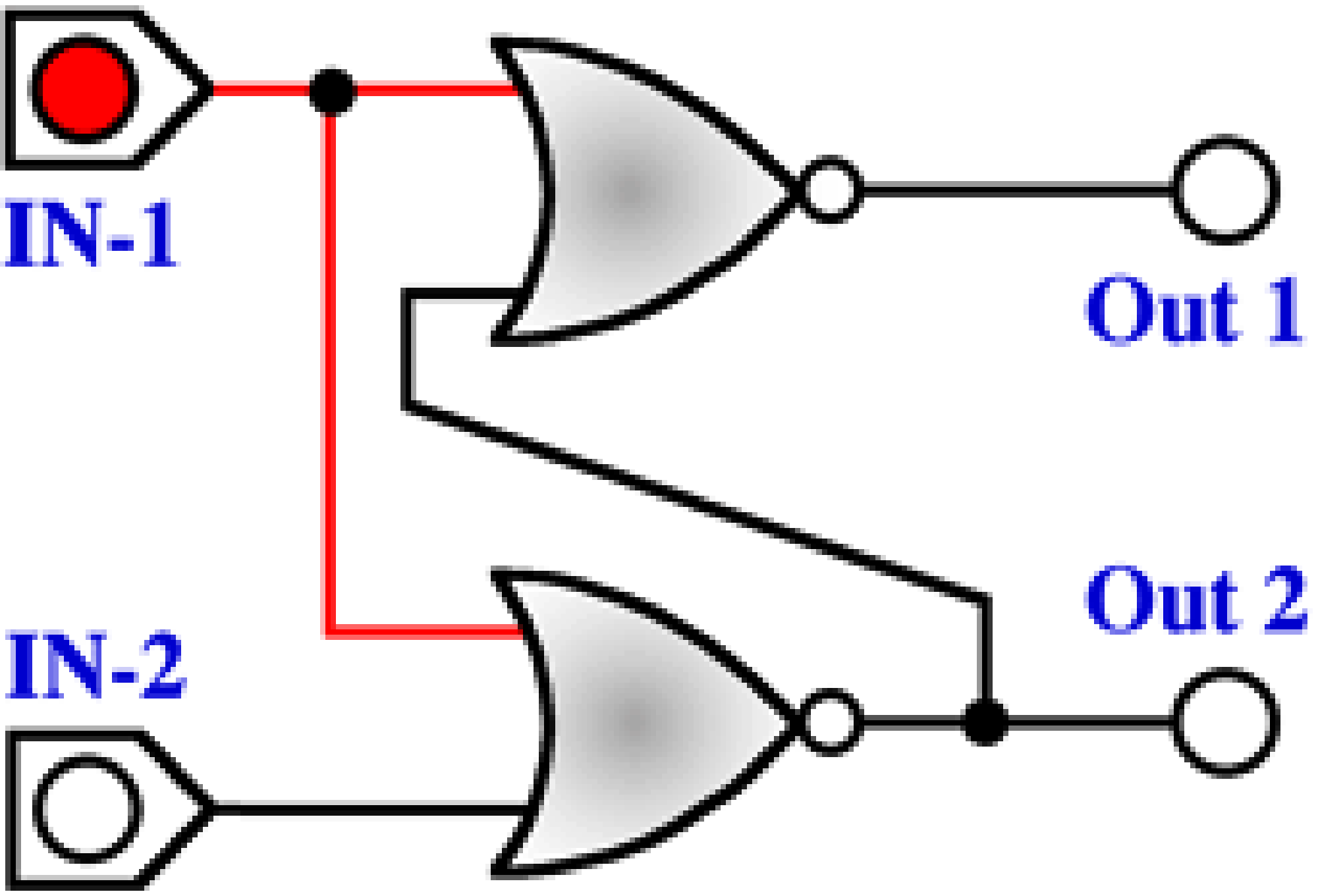
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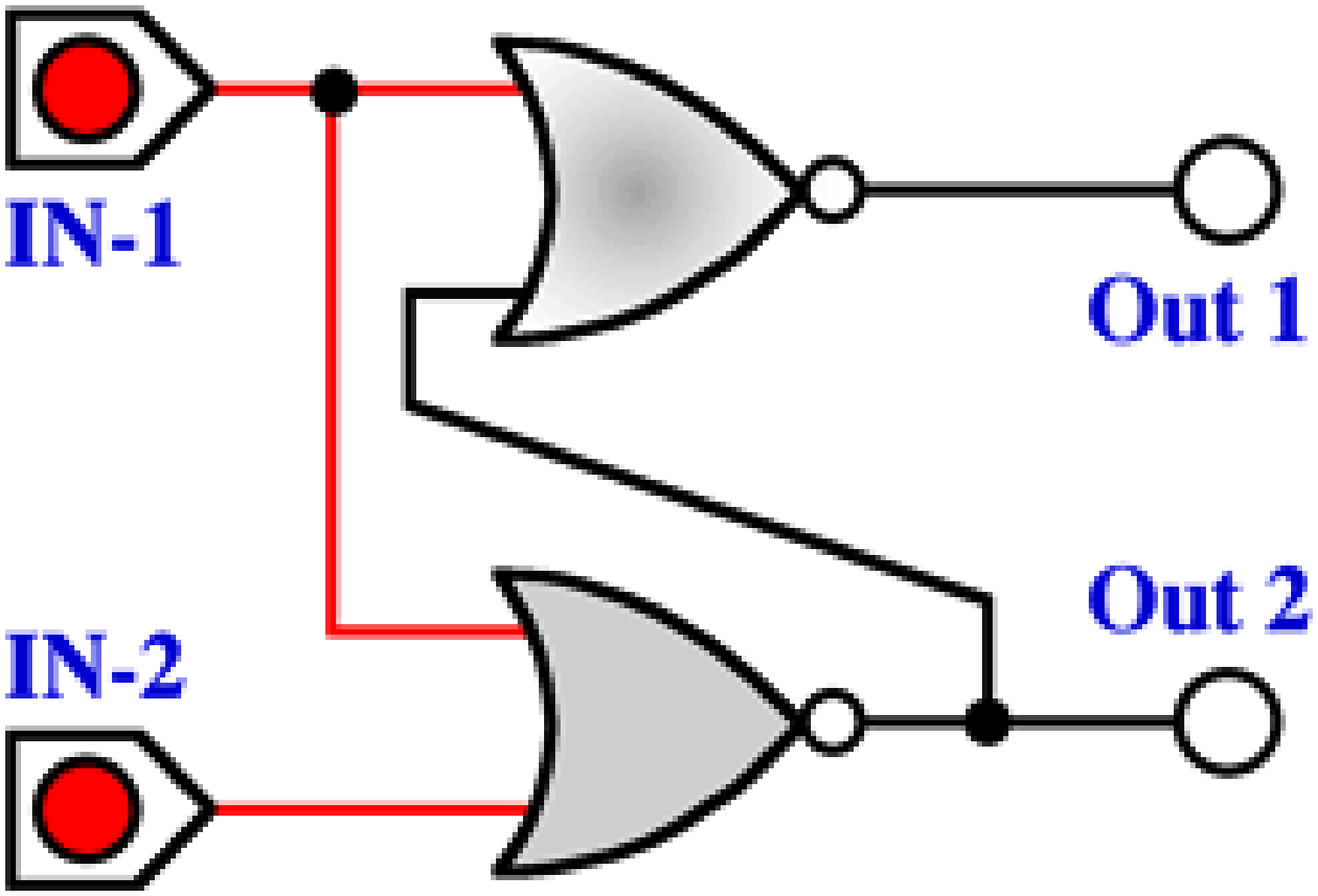
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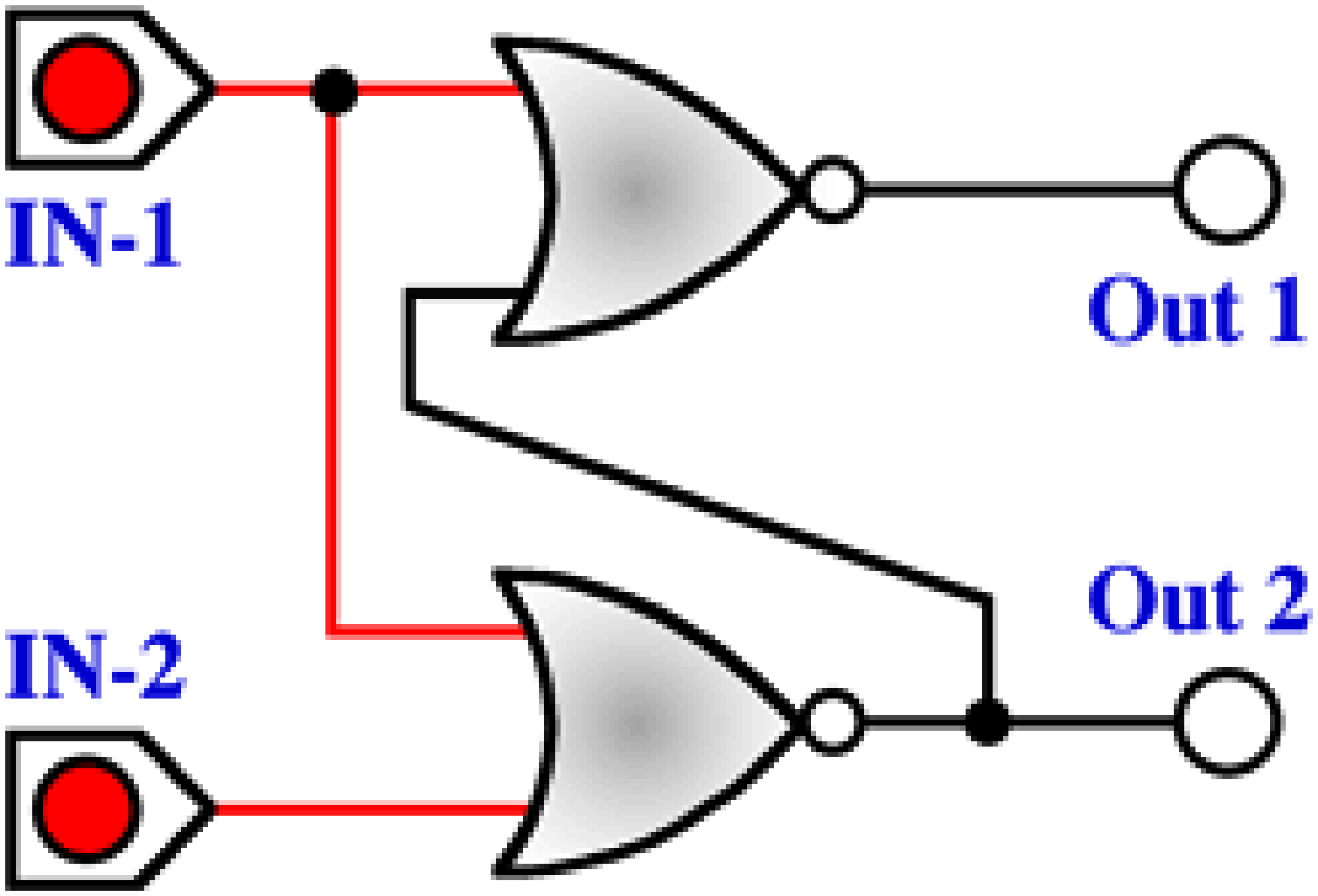
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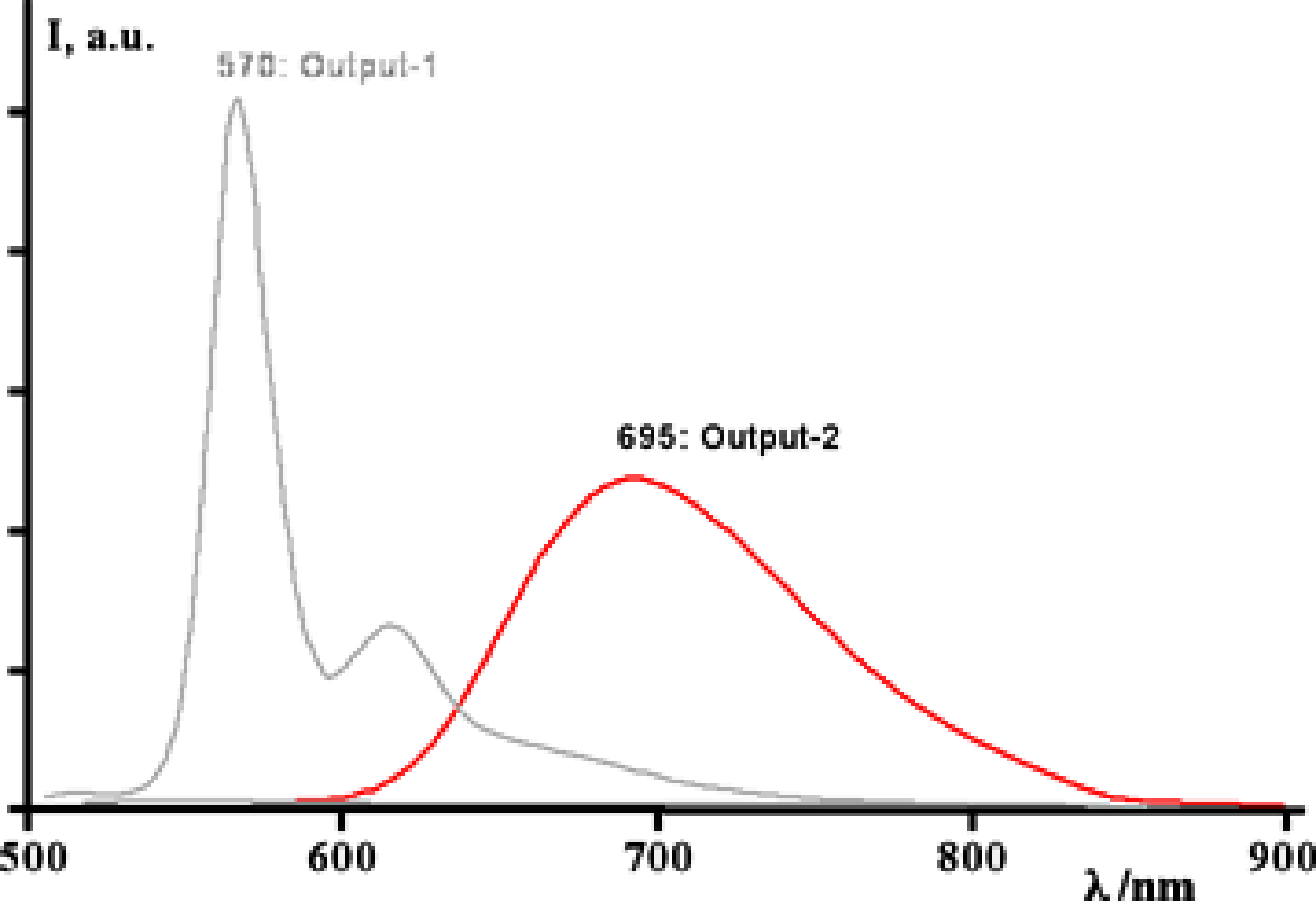
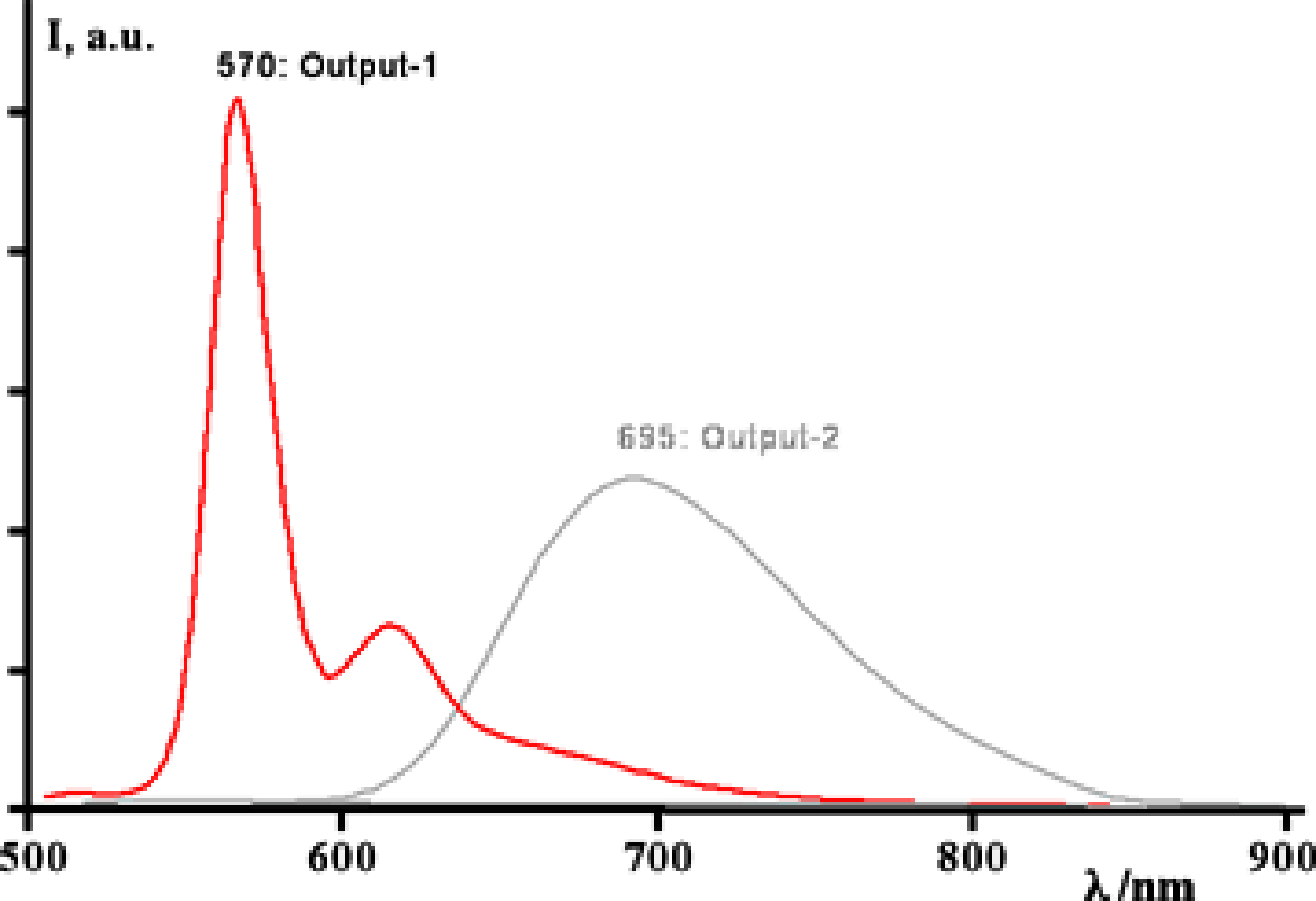

I, a.u.
570: Output-1
695: Output-2
500
600
700
800
900
λ/nm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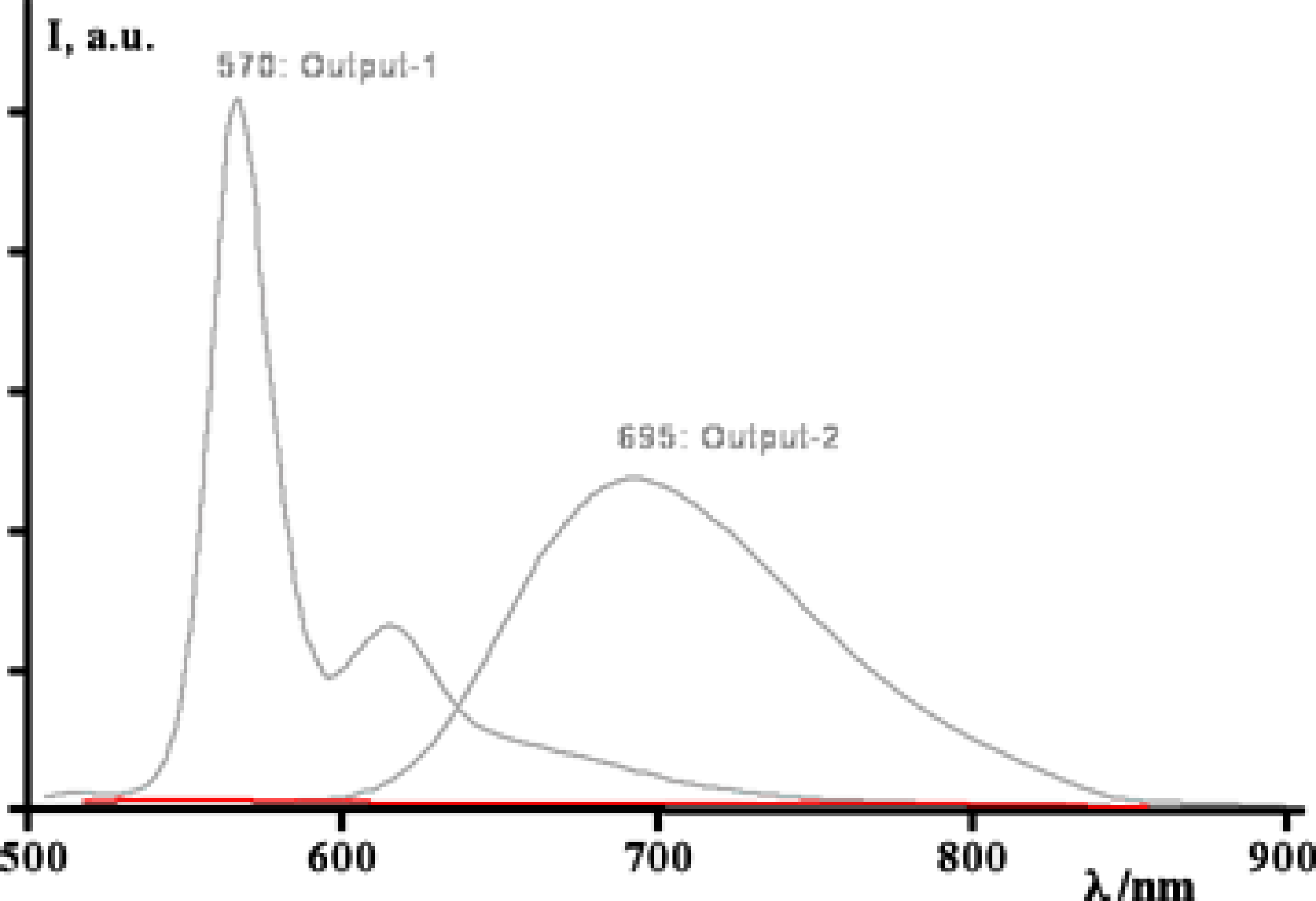
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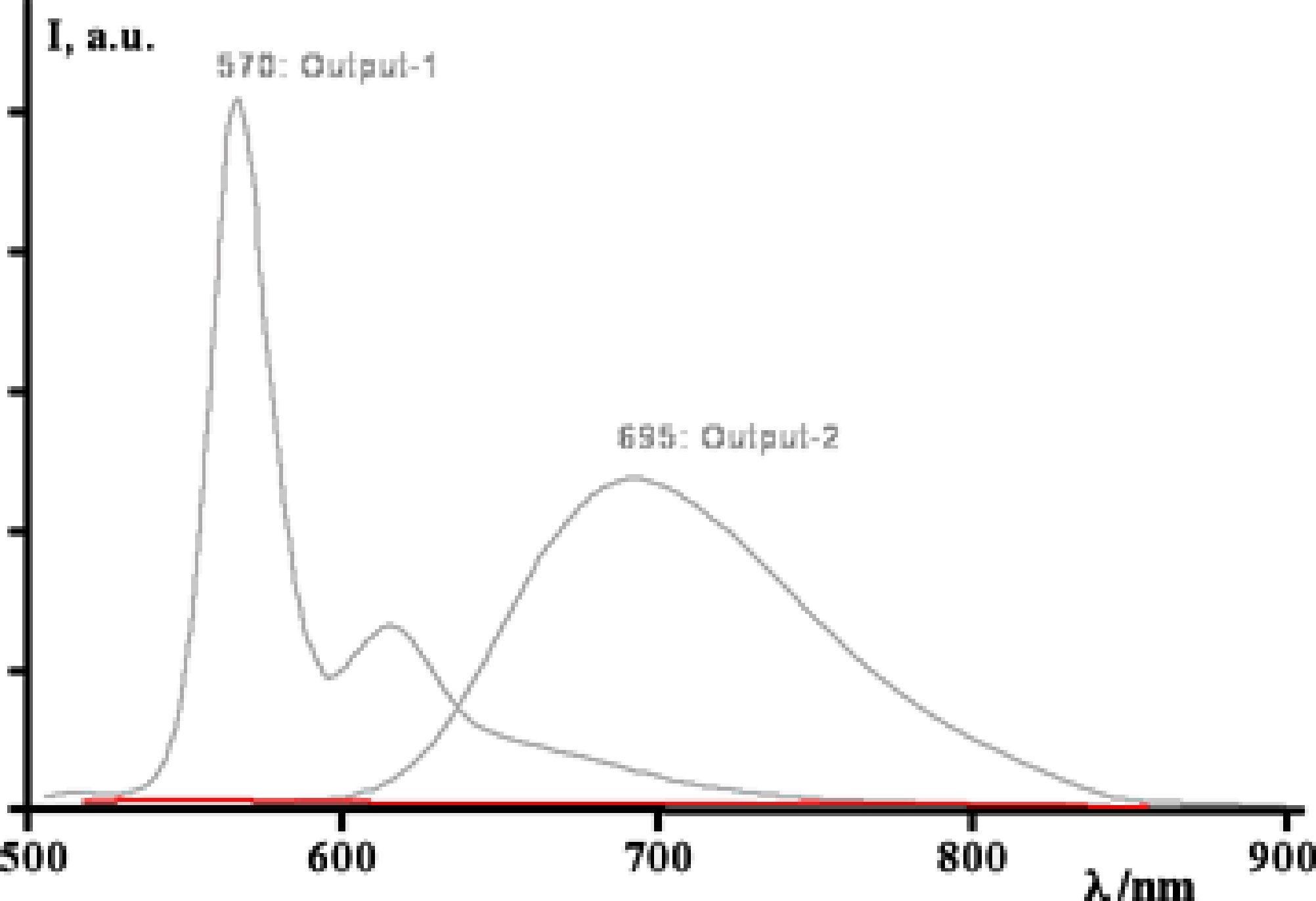
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Molecular logics: A mixed bodipy-bipyridine dye behaving as a concealable molecular switch

Fausto Puntoriero, Francesco Nastasi, Thomas Bura, Raymond Ziessel, Sebastiano Campagna, and Antonino Giannetto.*

SUPPLEMENTARY INFORMATION

TABLE OF CONTENTS

1) Synthetic protocol for the preparation of dye 1.

Our key molecule is compound **1**, shown in **Figure S1**, which comprises an extended fluorescent core made of a 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (Bodipy) dye, and a complexation pocket made of a tertiary amine tethered with two bipyridine subunits.

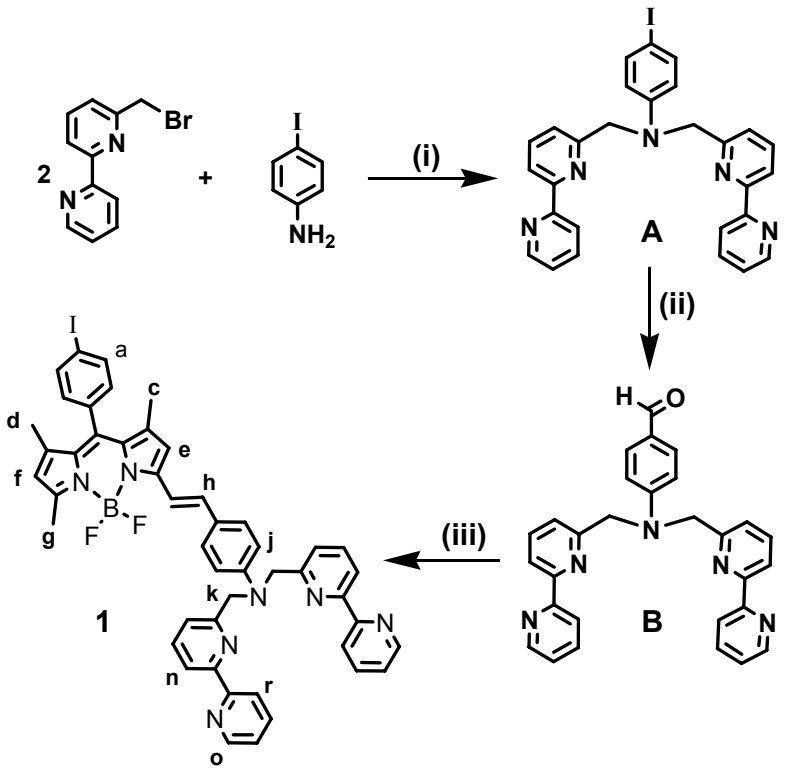

Figure S1. Keys: i) CH_3CN, KI 10 mol%, K_2CO_3 20 eq., 80°C, 5 d, 80%; ii) $[Pd(PPh_3)_2Cl_2]$ (10 mol%), HCOONa (1.2 eq.), CO 1 atm, DMF, 100°C, 3 h, 83%; (iii) toluene, piperidine, Dean-Stark, 65%.

Briefly the target hybrid dye **1** was prepared according to Figure S1 and the preparation start by alkylation 4-iodoaniline with 6-bromomethyl-2,2'-bipyridine[1] under anhydrous conditions providing **A** in acceptable yields. The key step is the formylation of **A** leading to **B**. Classical procedures (Villsmeir formylation, metallation and formylation, etc.) are not suitable in this case providing intractable reaction mixtures. The solution came from a carboformylation reaction[2] catalysed by Pd(0) under a flux of carbon monoxide with sodium formate as the hydrogen source that we recently disclosed.[3] The final step involves a Knoevenagel reaction catalyzed under basic conditions between 8-(4-iodophenyl)-1,3,5,7-tetramethyl-4,4difluoro-4bora-3a,4a-diaza-s-indacene and the formyl derivative **B**. The good selectivity found for the mono-substituted derivative versus the di-substituted compounds is controlled by the stoichiometry as well as the reactions conditions (temperature, reaction time and solvent composition).

References

1 R. Ziessel and J.-M. Lehn, *Helv. Chim. Acta,* 1990, **73**, 1149.
2 T. Okano, N. Harada and J. Kiji, *Bull. Chem. Soc. Jpn*. 1994, **67**, 2329.
3 T. Bura, P. Retailleau and R. Ziessel, *Angew. Chem. Int. Ed*., 2010, **49**, 6463.

2) The Interactive figure showing the behavior of 1 is reported on a different file.